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7 1970 NASA/GSFC Battery Workshop

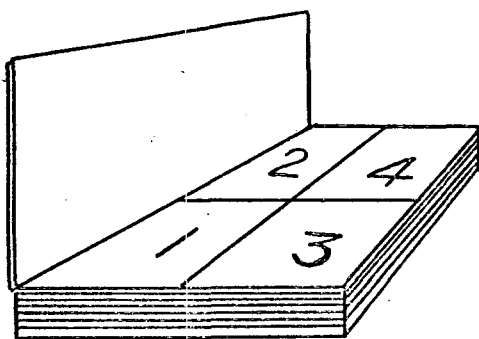
8 (Sessions 3 & 4)

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17 Goddard Space Flight Center,
18 Auditorium, Building 3,
19 Greenbelt, Maryland.

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21 Tuesday, 17 November 1970
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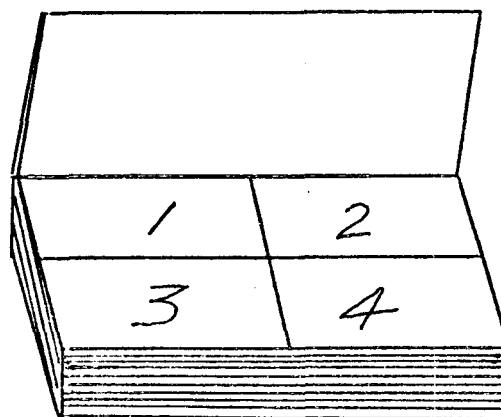
N O T E

IN GENERAL THERE ARE FOUR SLIDES PER PAGE. THE SLIDE SEQUENCE IS THE FOLLOWING, REGARDLESS OF BOOK ORIENTATION.



(Vertical)

FIGURE NO. 1



(Horizontal)

FIGURE NO. 2

C O N T E N T S

SESSION 3 =

PAGE

Separator Seals and Hardware

244 ✓

Chairman: T. Hennigan

SESSION 4 =

New Developments

351 ✓

Chairman: W. Billerbeck

SESSION 3

Separator Seals - Hardware

HALPERT: Good morning, gentlemen.

Starting this third session now I would like to introduce Tom Hennigan, Chief of the Electrochemical Power Sources Section here at Goddard. He has been actively engaged in battery technology for quite a long time, has considerable experience -- a very capable gentleman. I introduce Tom Hennigan.

HENNIGAN: Thank you very much, Gerry.

This morning, as you know, yesterday evening we had a couple of people who wanted to talk on accelerated testing and before we start on the separator - seals session here, we would like to have these two talks out of the way. I think they are about five or ten minutes in duration.

Of course, accelerator testing is one thing we sure would like to have every time we make a change in these cells we have to go through the same long life cycle test to compare it with the cells that we already have and today if you want to convince a project manager to change a cell or change the design of that cell you have to have this long cycle life test to prove to him that the battery is as reliable and as good as the ones that he flew before.

1 So our first speaker this morning will be Ed
2 Colston, who will give a rundown on some of the Battelle
3 work -- Design for accelerated testing.

4 Ed Colston is at Goddard Space Flight Center in
5 the Advanced Power Sources Section.

6 EDWARD COLSTON: I think it has become clear
7 with time that five or ten years of cycling is too long to
8 wait to find out you have a five or ten-year cell because,
9 for instance, we have some cells already craned now that
10 were put on in 1963 or 1964 which are excellent cells and
11 too bad they don't make those any more.

12 (Laughter.)

13 We are starting an updated Crane facility, as
14 you all have heard, and accelerated testing will be a part
15 of it. This is an outline, a very brief outline of some
16 of the philosophy involved and where we stand.

17 This work has been developing over the past
18 five years. We started out with contracts: RCA, Mauchly
19 Associates, the Crane Stat Group, and finally Battelle.
20 All of their reports were mailed out to the battery distribu-
21 tion list.

22 There is a tremendous amount of detail in these
23 reports. There is some smoke in parts of them, too. We
24 have reached a point where we are going to make some very
25 basic assumptions. We are going to assume that all aging

1 processes involve the physical movement of restructuring
2 of matter.

3 Two, that this aging is caused by one or more
4 of the following stresses: Gradients of temperature,
5 pressure, concentration or voltage. I was very pleased
6 to hear people talk about concentration gradients yesterday
7 perhaps causing some type of dendritic growth or potassium
8 oxide crystals being formed.

9 These stresses can generally be thought of
10 as thermal, mechanical, chemical, and electrical. We
11 have come up with on electrical quantity a calculatable
12 quantity we call Q. Finally, we have arrived at some-
13 thing we are going to describe as a number which describes
14 the goodness of a battery. We are going to call it Q.

15 In every case Q reduces to the units of
16 conductance per unit mass, mhos per gram. For instance,
17 a value which we will use in the Crane program is sort
18 of an electrical, a voltage quality. This Q_E is calculated
19 by taking one over delta voltage (ΔE) times the hourly
20 rate (n) times the grams per ampere hour (g').

$$Q_E = \frac{1}{(\Delta E \cdot n \cdot g')}$$

23 Grams per ampere hour, grams are measured.
24 Ampere hours are manufacturer's rated quantity. This is
25 the voltage quality.

1 We will assume that Q starts initially high
2 and degrades with time.

3 We will then take Q_0 -- Q sub zero -- and divide
4 it into the Qs at any point. (i.e. Q/Q_0)

5 This will give us a number between zero and one
6 which will initially start at one and decrease towards zero.
7 We will pick a point at which we will call it failed.
8 Probably it will be at or close to zero.

9 It is believed that the rate of decrease of Q
10 can be increased by combinations of the following independent
11 variables.

12 Note: These aren't necessarily stresses, pure
13 stresses. They are independent variables.

14 Environmental temperature, amount of overcharge,
15 rate of charge, depth of discharge, rate of discharge, and
16 there are about five others. Among them, vibration,
17 radiation, that sort of aging.

18 I like these because for the first five I
19 mentioned, four can be held constant while one is varied,
20 whereas if cell voltage is added, it can't be done. They
21 interact.

22 This Q ratio I spoke of between one and zero
23 is very necessary. Because, one, it allows us to
24 arbitrarily rate the goodness of a cell and, two, because
25 it arbitrarily points in the program, perhaps at Q values

1 of 1, .75, .50, and .25, to times at which sample cells
2 should be taken off line and analyzed. During the test program
3 in vivo analysis of live cells will be performed.

4 To date at Crane, when you take apart a dead cell,
5 you find a mass of gook with about fifteen things wrong with
6 it, and you don't know which caused what and what happened
7 together and what happened later because it was a dead cell
8 and you were running current through it.

9 The in vivo analysis will be to determine what
10 failure mechanism seemed to be progressing at what rate.
11 This is very important because accelerated testing means
12 that years of life testing have been simulated in a matter
13 of months, and the means in both cases by which it dies is
14 the same. The same failure mechanism or mechanisms must
15 dominate.

16 We can all take a cell and kill it in several
17 weeks. We can break it. Gross overcharge. Gross reverse
18 charge. Turn it into a balloon. Make it explode. But
19 what we have done to it is different than what it will
20 see in actual life. I don't think that the failure
21 mechanisms are the same. They must be the same for
22 accelerated testing.

23 From these values we hope to get an idea of
24 the sort of the failure mechanism or life cycle response
25 surface, to be able to correlate points. To be able to

1 correlate levels when the same failure mechanism exists,
2 the same general type of sensitivity to certain parameters,
3 an acceleration factor may be found say of ten; so that
4 instead of a year of testing, it takes 1.2 months --
5 although ten isn't a big enough acceleration factor; I
6 would like it to be about 100 or more.

7 It is proposed to use five levels for each stress.
8 It is proposed to use five basic cells per level plus cells
9 for teardown analysis. The full factorial experiment expands
10 quite rapidly. For one stress we need 55 cells. For two
11 stresses we need 260. For three stresses we need 2,165. Et
12 cetera. We cannot do a full factorial experiment for four
13 stresses or more. Therefore, we will do a partial factorial
14 test involving one to two hundred cells.

15 We will go through it using engineering judgment,
16 this sort of thing, previous Crane data, and what our predic-
17 tion techniques have come up with, to date, to eliminate and
18 reduce positions. We just can't afford 6,000 cells, especially
19 not built as tightly, uniformly, and with as much manufacturing
20 data as these cells will have to be made.

21 We will use our three analytical methods, the
22 general categories of analytical methods of the data that have
23 come forward so far. You have seen these pointed up in espe-
24 cially the last Battelle reports, the empirical, statistical
25 and physical ways of looking at data. We will hopefully get

1 an idea of the aging response surface. We won't do it all but
2 we feel that five points per stress is definitely enough to dis-
3 cover if one failure mechanism predominates. Three points will
4 give that if it's hopefully on a straight line. I don't think
5 that we will discover that -- it's purely temperature dependent
6 like a Arrhenius plot but five should be enough to tell you if
7 you have two.

8 Dr. Thomas, who acted as our statistician, assures us
9 that it will give us -- we can figure transition energies and
10 basically see if somewhere in the test range we are changing our
11 failure mechanism once. We hope to get years of data in months
12 and as prediction improves, right now our prediction technique,
13 as you have seen in the reports, is fairly good based on less
14 than a thousand cycles they have been able to predict a year,
15 two years, sometimes more, three years, of life based on less
16 than a thousand cycles. And this is with say 95 and 90 and up
17 percent accuracy.

18 As our prediction improves we hope to accelerate the
19 minimum number of cycles necessary to predict full life. In
20 other words, if we determine that with taking data this way and
21 with accurate data that based on 100 cycles, which isn't really
22 fully broken in, a cell which has a hundred cycles, we can pre-
23 dict its relative full life if we can accelerate this hundred
24 cycles into two days and then use this to predict the full life
25 of the cell in effect we will have a very powerful, if you will,

1 acceptance test. This is one way of getting meaningful accep-
2 tance tests. The ones that I have examined so far are effective
3 on picking infant mortality but beyond that it's very hard to
4 rate good, better, and best over life.

5 Now finally, my opinion of this work is that it has
6 made some very interesting, unusual, and useful contributions
7 to failure analysis, prediction, and I think that the Battelle
8 report made some, well, basic contributions to the theory of
9 the physical chemistry of aging.

10 Any questions?

11 (Applause.)

12 HENNIGAN: Any questions for Mr. Colston? Don't
13 forget to always give your name and association.

14 J. L. WEININGER: Weininger, General Electric.

15 I am sorry I am a little late, so I missed the
16 introduction. I'm really not sure whether this is the subject
17 of accelerated life testing. If it is, I have a few remarks
18 to make and slides.

19 HENNIGAN: I would like to introduce Dr. Weininger,
20 from General Electric, for a short talk on accelerated testing.

21 WEININGER: Actually, I got a number of topics I
22 should have liked to discuss a little bit anyway and specifi-
23 cally the business of accelerated life testing would have come
24 at the very end of it.

25 There is at GE a program sponsored by the Air Force

1 on increasing the energy density of nickel positive plates,
2 so this would be very appropriate to discuss now. But what I
3 was particularly interested in was in work which we were doing
4 at our laboratory last, which was the role of additives.

5 A few remarks seem to be indicated on that but
6 maybe not in this particular point of our discussions.

7 With regard to accelerated life testing, I recognize
8 how very important and thorough your testing must be in the
9 framework of what you are doing here but just to put a different
10 point of view on it, I would like to mention some wome work
11 that was done on this program which has a different approach.
12 And if I could have the first slide --

13 (Slide.)

14 The part I was concerned with particularly was the
15 role of additive in the nickel positive active material.
16 This is just a lift of the periodic table of all the additives
17 that have been put into the nickel positive plate, and
18 without going into details here, we go to the next slide, please.

19 (Slide.)

20 The purpose of discussing it in terms of life,
21 accelerated life test is that by having a certain voltage
22 scheme measuring the potential of the nickel positive plate
23 with respect to a reference electrode in the cell we can
24 simulate one single cycle by a triangular voltage step.

25 Assume now that this is a positive plate which you

1 have taken out of a battery. You increase under potentiostatic
2 control the voltage and let the current take its own value.
3 In that case you will find that you can cycle the plate,
4 or a small sample of the plate, and get some kind of
5 voltage trace like this, always under potentiostatic control,
6 but erratic, going up in voltage and down. And what I
7 am suggesting here actually is that you can compress 1,000
8 cycles of a charge, discharge operation into one weekend.
9 And the battery engineer has a great deal of difficulty to
10 consider this because they asked me actually what C rate
11 were you operating here, and if you consider the C rate by
12 the true definition of it, it is 100 C rate or a 1,000 C rate
13 when you discharge one amperehour cell for one hour you have
14 one C rate.

15 But when you discharge a ten milliamper-hour cell
16 for ten millihours you don't get a C rate but you still have
17 a 100 C rate. So what I am just saying is that if you just
18 stop aside for a moment and look at it differently, you can see
19 that you take the current densities at which you operate in
20 an ordinary C rate, take a little sample out of a battery
21 plate, and cycle it and within a few minutes, depending on your
22 sweep rate here, you can get a whole discharge charge cycle.

23 In our particular case we have done this specifically
24 to test -- I'm coming back now to the additive -- the case of
25 cobalt, where it was found that it is very beneficial to have

1 cobalt added to the nickel plate, particularly for the
2 charge acceptance and charge retention of the positive
3 at high temperature, high temperature being 45° C.

4 Maybe the next slide will show that.

5 That is just another sweep ratio oscillograph
6 trace. The next one, please.

7 (Slide.)

8 Here you see in two normal KOH and six normal
9 KOH what an electrochemically deposited nickel sample
10 will do in two normal and six normal KOH solution. The
11 Q here refers to the charge per square centimeter of
12 electrode. And it shows that relatively more charge
13 over longer periods of time is maintained where cobalt
14 is added to the nickel.

15 This is generally known in the battery industry,
16 but it's worth mentioning now also, and it's simply to show
17 you that it is possible to have some other accelerated life
18 test. And that's really all I want to say on that subject.

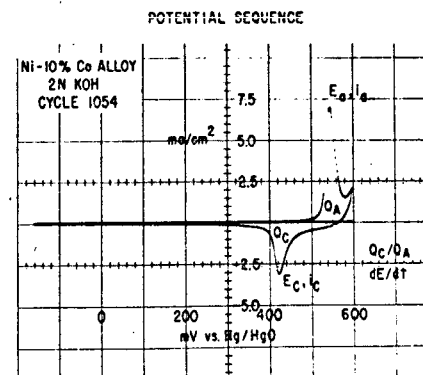
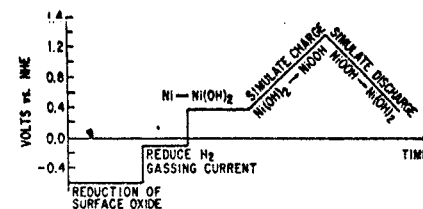
19 Thank you.

20 HENNIGAN: We have a question from Ernst Cohn.

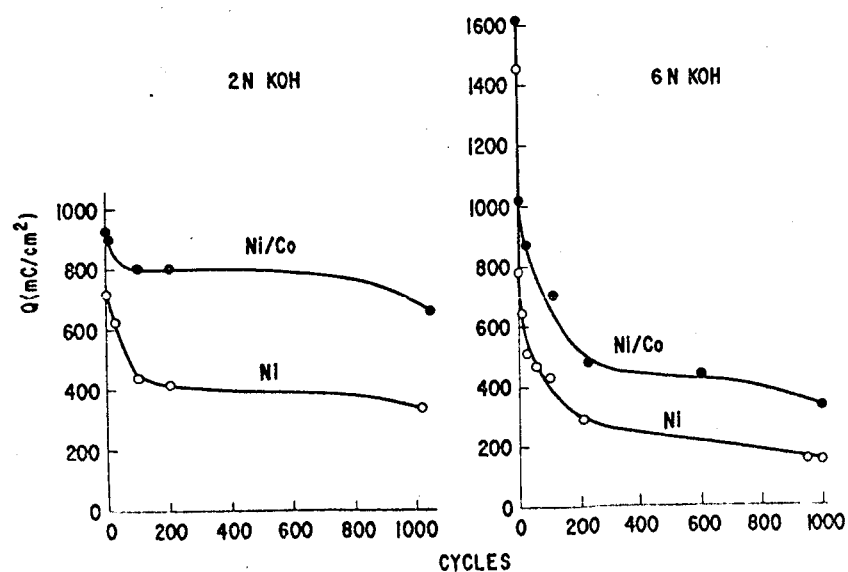
21 COHN: If you really believe that this is a good
22 method for simulating accelerated life testing, do you have
23 any plans for coordinating your sweep method with a true
24 regular life test to see how well they coordinate?

25 WIENINGER: Well, I'm afraid I'm in the R&D part

| | I | II | III | IV | V | VI | VII | VIII |
|---|----|------|------|------------|------|----|-----|------|
| 2 | Li | (Be) | B | | | | | |
| 3 | Na | Mg | (Al) | (Si) | | | | |
| 4 | K | Cu | (Zn) | Sc | | As | Cr | Mn |
| 5 | Rb | Ag | (Cd) | | Sn | Sb | Mo | |
| 6 | Cs | Ba | Hg | RARE EARTH | (Pb) | Bi | W | |



TYPICAL CYCLIC i vs. E CURVE FOR NICKEL



1 of this partnership. We have actually looked at the Crane
2 data and tried to see whether we can, at least the cobalt test,
3 whether we can correlate these with what is available in the
4 literature. If you are talking about actual commercial plates
5 that have been tested, there are no such tests available to us,
6 so the answer is essentially negative.

7 However, I think I would like to try this and
8 right now I am aware of the experimental difficulties I didn't
9 go into right now. What is involved really is if you have a
10 plate, just to punch out a small sample with the plate at a
11 couple of millimeters thick, a sample about one millimeter in
12 diameter and use this as your test electrode, and then all
13 I have to do is to wait for my colleagues to give up one of
14 their huge constant current potentiostats in order to be able
15 to really work at the current levels that are required.

16 I am aware of what has to be done but it hasn't been
17 done yet.

18 HENNIGAN: Do we have any further questions?

19 Sid Gross wanted to say a few words on accelerated
20 testing.

21 GROSS: I am going to waive it until next year.

22 HENNIGAN: Yes, you will have more data next year,
23 okay.

24 (Laughter.)

25 I'd just like to let the fellow know in the slide

1 room that we are starting the regular schedule now. This is
2 the regular setup for slides that we have lined up.

3 Our next session this morning is going to be on
4 separators, which is a very popular talk around the battery
5 business. Of course one of the problems with picking a
6 separator again is we don't have any real good test to tell
7 us how a separator is going to work in a battery. I will
8 show some data later that some of these wetting tests that
9 you wouldn't even pick these separators for worked quite well
10 in batteries. We don't know how long they are going to work.
11 There are some indications that the physical properties and
12 materials will tell you not to use certain types of separators.

13 The other problem we have is with supply of these
14 materials. It seems like every once in a while you come
15 across a pretty good one and it seems kind of difficult to
16 get the material again. The fellow went out of that business
17 or he changed the process or something. So pretty much I
18 guess the industry has stuck to the nylon type material,
19 primarily made by the Pellon Corporation, usually referred
20 to as 2505ML, and as long as the temperature is cold, or
21 at zero, we had pretty good success with that separator.

22 The trend now is to try to find a polypropylene
23 that will also work in the cells for long periods of time.
24 I don't know if it's going to allow us to raise the tempera-
25 ture in these cells because we are still probably going to

1 to have problems with the cadmium migration. I don't
2 think the Pellon will really stop it.

3 Let's get on to the few speakers we have this
4 morning in the separator area. Our first one is Mr.
5 Gary Lyons, from Howard Textile, who would like to talk
6 about some nonwoven polyamides, the physical and chemical
7 characteristics.

8 Gary Lyons.

9 GARY LYONS: Good morning, gentlemen. For those
10 of you that don't know me, my name is Gary Lyons, and I
11 am an officer of Howard Textile Mills, Allied Heat Seal
12 Corporation, and United Processing.

13 For the past twelve years we have been producers
14 of woven and knitted nylon cloth. We also have made
15 nylon envelopes for use as battery separators, and we
16 have recently produced a new 100 percent polypropylene woven
17 cloth of exceptional high strength and heat resistance,
18 about eight mills thick, and additional sample yardage
19 of these goods will be available very shortly for anyone
20 who is interested.

21 Since 1969 we have been working with Monsanto
22 Corporation in adopting Cerex for batteries. And in
23 1970 we were appointed distributors of Cerex to the
24 battery industry.

25 In recent years the use of man-made fibers in both

1 military and industrial applications have increased dramati-
2 cally. Many different fibers and a multiplicity of fabric
3 constructions are now available. Consequently fabric and
4 fiber constructions for specific end uses are selected after
5 meticulous assessment of their performance properties. Aware
6 of the need for a top performing fiber and new lower cost
7 structures, Monsanto, in 1963 began research on spun bonded
8 materials and this research has culminated in the development
9 and more recently in quantity production of Cerex spun bonded
10 nylon fabric.

11 Manufactured by an integrated process of fiber
12 spinning and bonding, Cerex is formed from a web of 100
13 percent nylon, 66 continuous filaments self-bonded at the
14 filament junctions. It contains no adhesive, no sizing,
15 binders, or fabric finishes.

16 On an equal weight basis, Cerex is the world's
17 strongest nonwoven fabric. It possess all of the high
18 performance attributes of nylon 66 plus the unique features of
19 a specifically engineered spon bonded structure.

20 Could I have the first slide, please.

21 (Slide.)

22 A scanning electron photomicrograph of Cerex
23 at 24 times magnification is in that slide number one. In the
24 figure there is a network of bonded continuous filaments with
25 genus ranging from three to five. Because of the absence of

1 any external binder it is possible to have a web of uncoated
2 filaments characterized by a high surface area with an
3 abundance of interstices for easy circulation of the electrolyte.

4 This may not be the case for the staple filament
5 woven where matted areas of fiber and binder diminish surface
6 area.

7 At this point it is important to note the difference
8 between spun bondeds and the broad class of products nonwovens.
9 Spun bondeds are continuous filament web, web structures,
10 bonded at the filament crossover points. The key word is
11 "continuous filament." The continuous filaments along with
12 strong bonds allows any external force to be propagated
13 throughout the fabric to a significant extent. This causes
14 Cerex to be much stronger than any staple fiber nonwoven.

15 Could I have slide number two?

16 (Slide.)

17 Cerex is also a highly homogeneous structure due
18 to the absence of an external binder. This is particularly
19 evident in slides one and two where the clean network of
20 Cerex filaments is contrasted with slide number two, a staple
21 nonwoven. Where discrete filaments are held together in a
22 contiguous network by globs of binder. The total nonfibrous
23 material content of Cerex is less than one percent. According
24 to Federal spec CCT-191B, Method 2611.

25 With no finishers or binder systems present

1 contamination hazards are reduced.

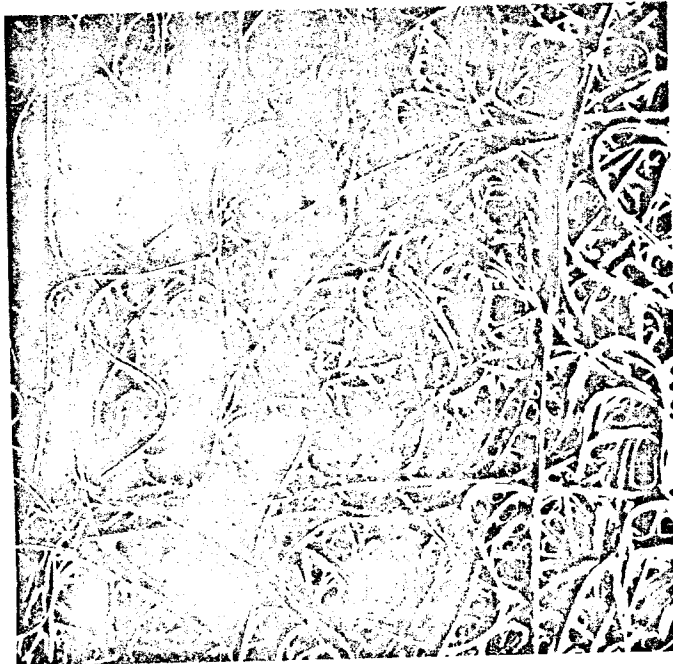
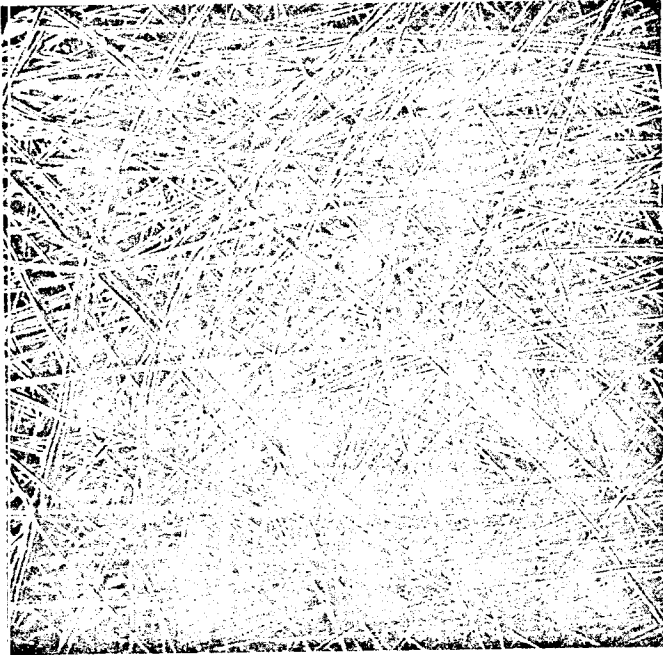
2 Could I have Table 1, please?

3 (Slide.)

4 The weights and typical physical properties of the
5 range of currently made Cerex styles are given in Table 1.
6 Cerex is being analyzed for end use properties specific to
7 batteries which use a potassium hydroxide electrolyte. For
8 this end use a low density material was developed to promote
9 higher electrolyte retention. Specifically electrolyte
10 retention in 30 percent KOH has been increased from approxi-
11 mately 200 to 700 percent with a low density fabric. As
12 expected some sacrifice in the mechanical properties was
13 experienced in going to a lower density fabric as the degree
14 of bonding was reduced. Specifically strip tensile strength
15 for low density fabric averages six pounds per inch for both
16 machine and transverse directions versus 25 pounds per inch
17 for standard fabric. Mullen burst strength still exceeds 50
18 pounds per square inch. Elongations have been lowered in both
19 directions from 80 to 25 percent.

20 Even with the sacrifice in mechanical properties
21 we believe low density Cerex to be as strong as any staple
22 nonwoven used for battery separators.

23 Although some reduction in wettability has been
24 achieved with a low density fabric further modifications are
25 now being made to improve this property.



NOT REPRODUCIBLE

TABLE 1. STANDARD CEREX® SPUNBONDED NYLON—WEIGHTS AND TYPICAL PHYSICAL PROPERTIES DATA

| Weight oz./yd. ² | Denier gms./9000 | Melt Strength (b) | Cash Strength (b) | Tensile (b) | Thickness (b) | Tensile (b) |
|--------------------------------|---------------------|-------------------------|-------------------------|----------------|------------------|----------------|
| 0.4 | 1,400 | 10 | 8 | 1.6 | 4 | 5 |
| 0.6 | 900 | 16 | 15 | 3.0 | 5 | 8 |
| 0.7 | 830 | 23 | 17 | 3.4 | 6 | 9 |
| 0.85 | 740 | 27 | 23 | 4.6 | 7 | 11 |
| 1.0 | 660 | 30 | 27 | 5.5 | 9 | 12 |
| 1.5 | 450 | 46 | 41 | 11.2 | 11 | 18 |
| 2.0 | 360 | 60 | 56 | 14.2 | 14 | 23 |
| 2.5 | 270 | 70 | 71 | 17.6 | 17 | 32 |
| 3.0 | 210 | 94 | 97 | 24.0 | 20 | 39 |
| 4.0 | 170 | 125 | 120 | 31.0 | 25 | 52 |
| 5.0 | 140 | 153 | 153 | 36 | 30 | 70 |
| 6.0 | 110 | 153 | 192 | 39.4 | 36 | 90 |

Properties Not Affected by Fabric Weight
 Recovery from Extension—Elastic recovery is uniformly high irrespective of fabric weight (see Fig. 2).
 Melting Point—In range 498–509 F (259–265 C)
 Color—Brightness, 75.3, purity, 0.1, dominant wave length, 513 mμ (As measured on G. E. Tristimulus Photometer.)

Notes: 1. Properties are typical values and should not be considered as absolute values or specifications.

2. Properties are typical values and should not be considered as absolute values or specifications.

3. Properties are typical values and should not be considered as absolute values or specifications.

4. Properties are typical values and should not be considered as absolute values or specifications.

5. Properties are typical values and should not be considered as absolute values or specifications.

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7. Properties are typical values and should not be considered as absolute values or specifications.

8. Properties are typical values and should not be considered as absolute values or specifications.

9. Properties are typical values and should not be considered as absolute values or specifications.

10. Properties are typical values and should not be considered as absolute values or specifications.

1 Thank you. Are there any questions.

2 (Applause.)

3 HENNIGAN: Thank you very much, Gary.

4 MAURER: Maurer, Bell Laboratories.

5 Can you make spun bonded polypropylene?

6 LYONS: We can and we probably will. We're working
7 on it now.

8 HENNIGAN: Thank you, Mr. Lyons.

9 Do we have another question?

10 FALIK: Andrew Falik, from Monsanto.

11 If the market justifies the spunbonded polypropylene
12 we could go commercial. Now it's like any other organic
13 polymer, one of many that we are trying to make in spunbonded.
14 At the present it's not amenable to a spunbonded process,
15 polypropylene.

16 HENNIGAN: Thank you very much.

17 Sid Gross of Boeing?

18 GROSS: Gross of Boeing. My understanding is that
19 nylon, there are many kinds of nylons of different molecular
20 weights and presumably of different stabilities in electrolytes.

21 What can you say about the differences between
22 spunbonded nylon and other Pellon type nylons in this regard?

23 LYONS: Well, our spunbonded nylon is a 66 nylon
24 which would have perhaps marginal or even significant greater
25 resistance to degradation in alkaline solution. But pellon,

1 I'm not sure, perhaps it's a nylon 6 polymer, so we would expect
2 with the difference in the polymer characteristics a little
3 less resistance to a heavily alkaline solution.

4 As far as other nylons, there is no other nylon spun-
5 bonded being made. We feel as far as resistance goes Cerex
6 would probably have the highest resistance to an alkaline solution
7 of any nylon nonwoven being currently made.

8 HENNIGAN: Are there any more questions on this
9 nylon?

10 Bob Steinhauer of Hughes?

11 STEINHAUER: Yes, I would like to ask, we have been
12 concerned about separator degradation and particularly the
13 nylons and hostile formation of carbonate. Would these spun-
14 bonded nylons contrasted to the unwoven materials be more
15 resistant? In other words are these binders the things that
16 are breaking down rather than the nylon itself?

17 FALIK: Pellon advertises, and I believe rightly
18 so, 100 percent polyamide structure. We also advertise 100
19 percent polyamide structure subject to the solvent, of
20 extractions with water and chloroform plus the ash content
21 which is less than one percent, which I don't think Pellon
22 could exceed that figure either.

23 I feel that as far as degradation is concerned,
24 it's a question of nylon 66 versus nylon 6 and this would be
25 the only difference in the two materials.

1 HENNIGAN: Guy Rampell of General Electric.

2 RAMPELL: Can you tell me what air permeability
3 range of the commercially produced is at the moment?

4 FALIK: For our low density material style that
5 we hope will be used in battery separators it ranges from 300
6 to 350 cubic feet per minute per square foot of fabric at a
7 half-inch water pressure.

8 RAMPELL: Thank you.

9 HENNIGAN: Another question here -- Menard of
10 Gould.

11 MENARD: Do you have any binder in your fabric?

12 FALIK: There is no binder material in our
13 fabric. This is to say that if we took a staple nonwoven
14 and subjected it to a solvent extractions and water extractions
15 and ash and we took our material, we -- the total amount of
16 -- there would be nothing in the extractions that would be
17 representative of any binder.

18 MENARD: You mentioned about Pellon being 100
19 percent nylon. They do have the binder which is zinc oxide
20 in there. We ran analysis some years back and I think this
21 is what caused the degradation -- the binder itself, not the
22 nylon fibers.

23 I don't know if there is anybody here from Pellon
24 who would like to comment on this.

25 HENNIGAN: I believe that's zinc chloride, isn't it?

1 MENARD: Where does the zinc come from?

2 HENNIGAN: Do the fellows from Pellon like to say
3 anything about that?

4 VAN BEAVER: Van Beaver of Pellon Corporation. The
5 binder system is proprietary. I cannot comment on it.

6 But I would like to ask Monsanto a question on the
7 binder.

8 (Laughter.)

9 FALIK: It's proprietary.

10 VAN BEAVER: Right.

11 (Laughter.)

12 VAN BEAVER: Then you do have a binder in your
13 system.

14 FALIK: No, sir.

15 VAN BEAVER: No binder whatsoever?

16 FALIK: No.

17 HENNIGAN: Sid Gross from Boeing?

18 GROSS: Gross, Boeing. Of particular importance
19 of course is the ability to make separator very uniform and
20 very predictable and very consistent.

21 Could you -- do you have any remarks on what
22 performance you have experienced in this regard?

23 FALIK: I feel our spunbonded would not be worse
24 than any other commercially nonwoven that is available on the
25 market now. We certainly at this time could not make as

jrb-23

1 uniform a material as a woven structure. I don't feel that
2 any nonwoven producer has a plus as far as uniformities are
3 concerned.

4 I would like to point out we have a big program
5 in measuring uniformity and it is a function of how many samples
6 you take and the area over which they are taken. From this
7 conference perhaps I would like to get an idea of how you
8 would want us to sample uniformity in a battery separator
9 material. Should we take three-inch squares and measure them
10 for density and weight and do a thousand of these within a
11 thousand yards across a 50-inch width, or do we use a six-inch
12 width so if we come up with some variation statistics they
13 could be more meaningful?

14 HENNIGAN: Could we have the spelling of your
15 name, sir?

16 FALIK: Yes, it's incorrect on there. It's
17 F-A-L-I-K.

18 HENNIGAN: Mr. Rampell from GE has some information
19 on degradation of Pellon in KOH. Do you want to say anything?

20 RAMPELL: You are talking nylon. Hans Krøger, Dr.
21 Krøger ran some permanganate oxidation tests and of course
22 nylon does degrade and oxidize under those conditions. And
23 he also ran 160 degree Fahrenheit storage tests in electrolyte,
24 31 percent electrolyte, and found that -- well, it was almost
25 impossible to find any nylon at the end of the storage period

1 which was about six months. And in contrast to that,
2 polypropylenes are about the only materials that survived and
3 also were practically non-oxidizable in the potassium perman-
4 ganate.

5 HENNIGAN: I guess you well know when these cells
6 are run at say 40 degrees C in less than a year, there just
7 isn't any separator left. I mean it's completely gone. It's
8 a piece of mush in there with cadmium all mixed in with it.
9 So at .25, it goes, depends on how you used the cell, in two
10 to three years, zero. We had these nylon cells with the nylon
11 in it running for six, going on seven, years.

12 Gary Lyons?

13 LYONS: I presume that when you say that there is
14 no nylon left you are referring to nylon other than the Cerex
15 spunbonded? I don't believe that that has disintegrated under
16 heat in any test that you have made.

17 HENNIGAN: That we made?

18 LYONS: That have been made.

19 HENNIGAN: Oh.

20 Are there any further questions?

21 Dr. Maurer from Bell?

22 MAURER: I have a few general comments, We have
23 been doing some accelerated aging studies. Our use mode for
24 cells in many instances is long term overcharge at elevated
25 temperatures. And we have an accelerated test program

1 along those lines that I think we will report on at the power
2 sources conference, but it involves several hundred cells at
3 different overcharging rates and temperatures.

4 Our general feeling is that nylon 6 and also
5 nylon 66 are degraded in oxygen KOH environments, and essen-
6 tially agreeing with what Guy Rampell has said on nylon in
7 permanganate KOH solution. It's our opinion at Bell Labs
8 that a long life cell must not contain any nylon at all.

9 HENNIGAN: Thank you.

10 We will go on to our next -- do you have a question
11 over there?

12 HALPERT: Halpert, Goddard.

13 I am not sure as to the relationship of the test
14 in the hot KOH and the oxidizing atmosphere as compared
15 with the environment the separator experiences inside the
16 cell. That is, if you take the separator and measure its
17 thickness with a Caty gauge you get 14-15 mil on the maximum
18 loft material, which is the type used inside the OA0 type
19 cells. Then, after plates and separator are pressed and
20 the pack inserted into the case, if one determines the room
21 left for the separator we find the thickness may be seven
22 or eight mil.

23 After a long term cycling we find the plates
24 themselves have increased in thickness, the positive in
25 particular have increased by 5 mil apiece. So we really

1 are doing one other thing inside the cell. We are stressing
2 in terms of force.

3 That might be one of the other things we want to
4 consider in this accelerated test work.

5 HENNIGAN: Bill Ryder from Gulton??

6 RYDER: I just want to ask a question of Dr.
7 Maurer.
8

9 When you say long life, do you mean twenty-five
10 years on cycle, your typical standby power system life
11 requirement on batteries, or are you referring to space type
12 of service?

13 MAURER: I am referring to greater than five years
14 at toom temperature.

15 RYDER: Standby power, constant trickle charge,
16 long life.
17

18 MAURER: Yes.

19 RYDER: Thank you.

20 HENNIGAN: Dr. Weininger, did you want to say a
21 few words on separators?

22 WEININGER: Yes, but I again have some slides to
23 show.

24 HENNIGAN: Okay.

25 WEININGER: I have a few electron micrograms to

1 The ridges and striations are artifacts from the slicing of
2 the sample. This one is a polyethylene. The next slide shows
3 a polypropylene.

4 (Slide.)

5 Again very small pore sizes. There is a hole there
6 from the slicing, a tear, actually. Next slide please.

7 (Slide.)

8 Just because at that time, at the Battery Separator
9 Symposium we were very interested in what was considered to be
10 the best alkaline battery separator, the RAI grafted poly-
11 ethylene. We made one particular electron micrograph on
12 RAI with very high conductivity, and this particular sample had
13 pores also. These are less rounded more gene-like structures --
14 are pores in RAI separated, but I don't want to give you the
15 impression that they usually have pores. I only want to
16 demonstrate this particular one because it was very heavily
17 radiated in their process I suppose and pores develop.. I can
18 assure you that all other RAI separators we tested didn't
19 have actual holes of this nature. But even if they had, the
20 pore size is here only on the order of 100 angstroms itself.
21 And that is not necessarily detrimental. In fact when you
22 come to an ion exchange membrane you arrive at the question
23 of what fractional pore sizes of the molecular level of an
24 ion exchange membrane really is.

Now these separators are cheap to make, they are

1 show you of the new porous polyethylene membrane, porous
2 polypropylene membrane, also, and all the things of highly
3 crystalline polymers of this nature and these polymers are 50
4 percent porous and have the distinction of having very small
5 average pore size of average of 60 to 100 angstroms.

6 The first slide shows you a distribution of these
7 pore sizes. This has been actually published in the Journal
8 of Electrochemical Society and also at greater length in the
9 Proceedings of the Battery Separator Symposium at Columbus last
10 spring.

11 I would to bring it to your attention at this time.
12 Could I have the first slide, please?

13 (Slide.)

14 The next one, please.

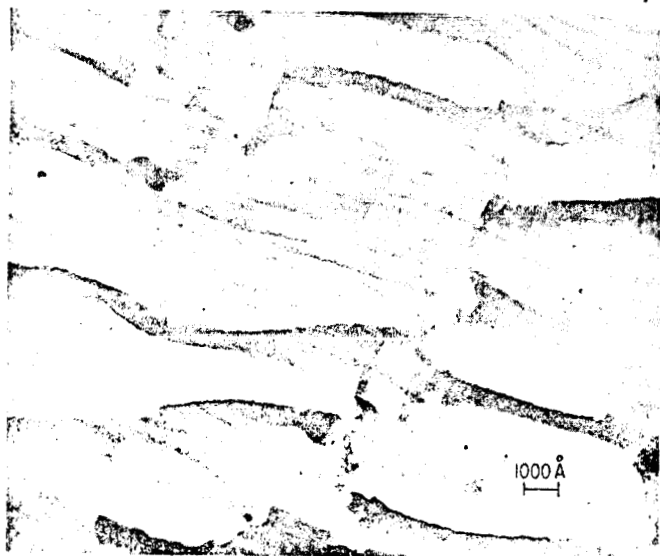
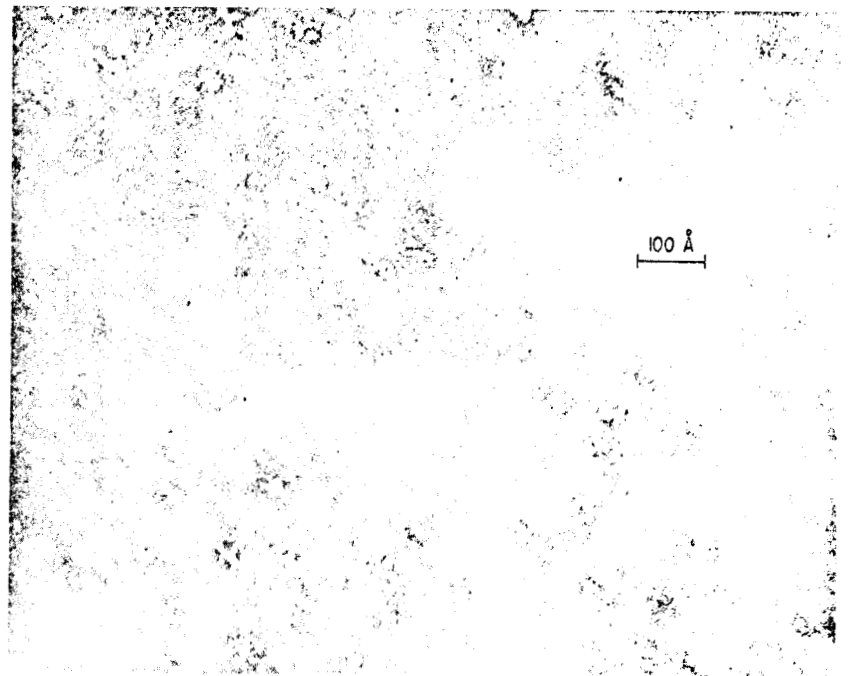
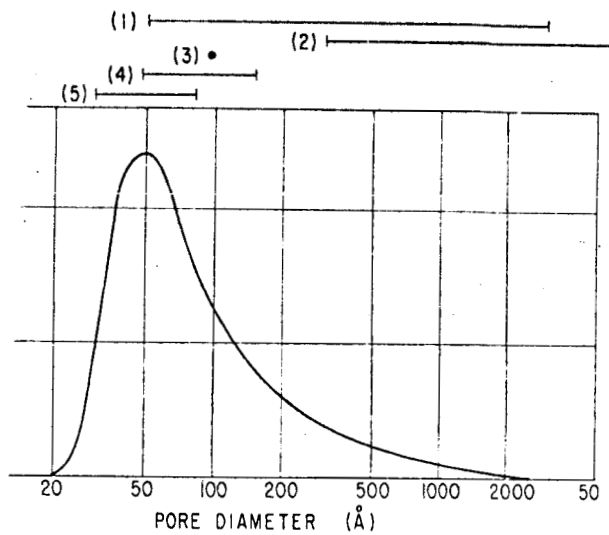
15 (Slide.)

16 Without going into any details on the methods by
17 which we established these pore sizes, this is a 50 percent porous
18 polyolefin, it has a few large pores, but the majority you can
19 see are smaller than 100 angstrom in pore size.

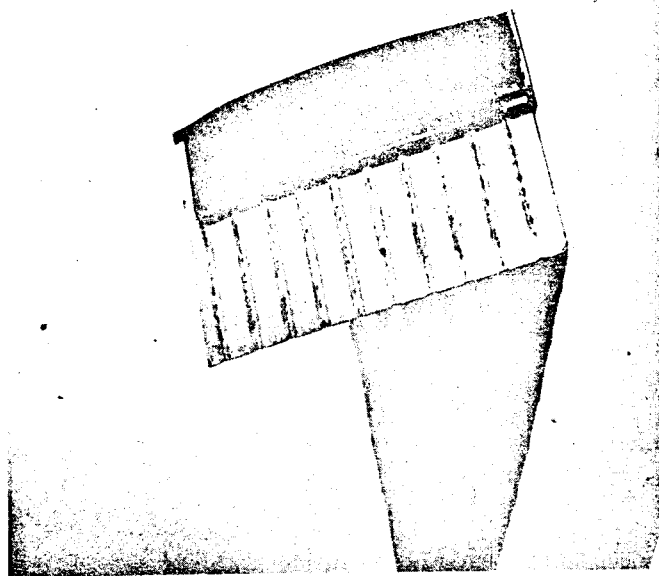
20 One of the methods of determining these is shown
21 in the next slide.

22 (Slide.)

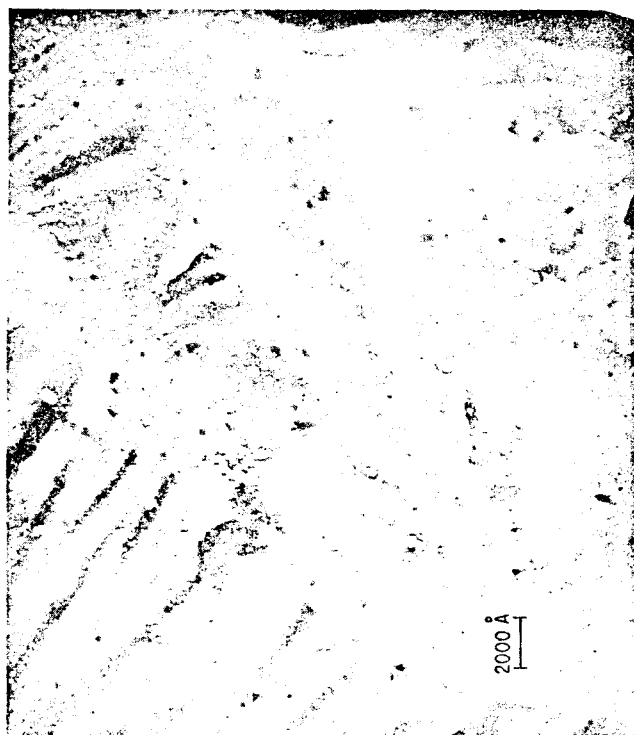
23 You see an actual electron micrograph of a section
24 of this polymer. Now these little dots or water marks as they
25 appear are actual pores. The largest one there is 200 angstroms.



NOT REPRODUCIBLE



NOT REPRODUCIBLE



1 100 percent polyethylene. There is no additive to it. As a
2 result they have a peculiar property of being completely
3 hydrophobic. And they will not allow water to come in
4 unless it is placed there in the first place. They can be
5 heat sealed very readily and a number of battery applications
6 and many more that are not related to battery technology.

7 Whether or not they would be useful in alkaline
8 batteries is a question but I just mention one other parameter,
9 and that is the tortuosity which is about three-to-ten;
10 average tortuosity of seven, let us say. So depending on the
11 thickness you have, you see you decrease your effective
12 conductivity considerably. If you have applications with
13 reasonably low drain, meaning no higher than one or two C,
14 this might be a good alkaline battery separator.

15 Without question it is very good for a lead acid
16 cell. And the next slide will show you just one example of what
17 is a convention lead acid battery separator, the brown card-
18 board resin impregnated type behind there on which we have a
19 lead plate, positive plate, I believe, which is just slid into
20 a bag made from this material.

21 That's all. Thank you very much.

22 HENNIGAN: We had a question in the back there.

23 FALIK: Andy Falik, Monsanto.

24 If it's completely hydrophobic material then would
25 you care to comment on its wet-out properties?

1 WEININGER: The case of an alkaline system which you
2 have to have in the flooded state or enclosed in a fairly
3 humid atmosphere. In the case of the lead acid cell, the
4 sulphuric acid system, you have, as you look at the diagram
5 $\text{SO}_3\text{H}_2\text{O}$, you have a number of hydrated compounds which
6 the sulphuric acid is so heavily hydrated that it will not
7 dry out under any conditions, but there is no detergent or
8 anything else added to it.

9 HENNIGAN: Van Beaver of Pellon?

10 VAN BEAVER: Gerry Halpert approximately a week ago
11 cautioned me that there should be no sales pitches made at
12 this conference but I want to clarify two points:

13 One, Pellon has been marketing spunbond nylon for
14 approximately three years now.

15 Two, we understand and are fully aware that nylon
16 has limitations in long life and high temperature requirements.
17 For this reason we are pursuing and pursued polypropylene for
18 approximately nine year.

19 Thank you.

20 HENNIGAN: Well, I would like to get on to our next
21 speaker, who is Mr. Dangel, Mr. Phoenix Dangel from Kendall
22 Company, Fiber Products Division, on nonwoven separators.

23 DANGEL: Thank you.

24 Good morning. The Kendall Company manufactures non-
25 woven fabrics by the staple fiber system as distinguished from

1 the continuous filaments that were described earlier.

2 What I am going to talk about this morning is the
3 selection of textile fibers and fabricating techniques for
4 separator design.

5 The relatively new art of manufacturing fabrics
6 directly from fibers has permitted a design flexibility not
7 previously available with older techniques. The new class of
8 materials has been termed "nonwoven." The ASTM defines them as
9 follows:

10 "Fabrics, nonwoven. A planar structure produced
11 by the bonding or interlocking of textile fibers,
12 or both, normally accomplished by mechanical
13 work, thermal treatments, chemical or solvent
14 action or combinations thereof."

15 In the usual fabric manufacture that has gone on
16 for ages, fibers are first made into yarn, either by spinning
17 or twisting of short fiber hairs, or by continuous extrusion
18 of infinite length multifilament or monofilament strands. The
19 yarns are then either woven or knitted into fabric structures.
20 These have a thickness at least as great as the diameter of
21 the yarn and the porosity is usually a function of the actual
22 spaces between the yarns in the structures.

23 The first two slides will illustrate what I am
24 talking about.

25 (Slide.)

1 There is a typical woven structure and the next
2 slide (Slide) is a typical knitted structure. All right, you
3 can take the slide off, please.

4 In the case of the nonwoven fabrics, thickness and
5 pore size are usually more closely related to the diameters of
6 the individual fibers, the number of fibers superimposed on
7 each other -- that is, the thickness of the sheet -- and the
8 processing history of the nonwoven. That is, the moduli of
9 rigidity and elasticity influence the fiber's behavior in
10 the final configuration as it is transformed into a nonwoven.

11 In fact, it is possible systematically to exploit
12 the chemical and physical natures of the fibers as well as the
13 geometric configuration in the deliberate design of a nonwoven
14 fabric to be used as a separator and electrolyte absorber.

15 Let us consider the factors involved in the design
16 criteria of a separator for a specific end use.

17 The first choice must be to select a fiber of
18 proper chemical and physical characteristics. The considerations
19 would include those shown in the next slide.

20 (Slide.)

21 Non-solubility and non-reactivity in acidic, basic
22 or organic electrolyte; resistance to oxidation or reduction;
23 swelling or shrinkage in electrolyte; and thermal stability.

24 Next must be considered the geometric characteristics
25 desired in the finished nonwoven fabric. These are shown in

1 the next slide.

2 (Slide.) Here we must consider fabric thickness, pore
3 size and shape; uniformity of pore size distribution; strength
4 in the X and Y directions; and elongation.

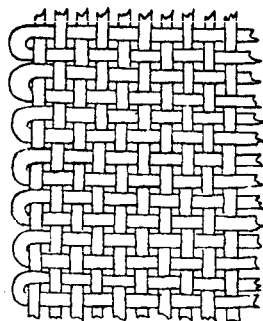
5 Now let us attempt the spatial geometry for this
6 hypothetical end use. Let us assume that we have chosen the
7 proper fiber, having considered all the factors in Table 1.
8 The next decisions must be how to array the fibers and to hold
9 them together to unify the sheet.

10 Basically, textile machinery in current practice can
11 either manipulate the fibers mechanically and lay them sub-
12 stantially parallel; or deposit them, usually from an air
13 stream in a random manner.

14 (Slide.)
15 The next slide illustrates the parallel array of
16 fibers in the machine direction, and the next slide in the
17 cross direction. (Slide.)

18 These structures are characterized by high strengths
19 in the direction parallel to the fibers and less strength in
20 the cross direction; and by quite uniform deposition of fibers
21 resulting in relatively uniform pore size. The illustrations
22 are, of course, idealized and the actual fabrics are not quite
23 as uniform as shown.

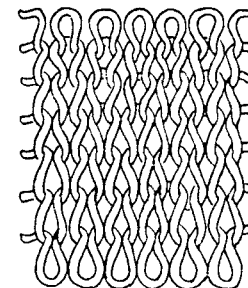
24 The next slide (Slide) illustrates random arrange-
ment of fibers, which may be either short lengths -- that is
staple fiber -- or continuous filaments, as described earlier



FIBER CHARACTERISTICS

- NON-SOLUBILITY AND NON-REACTIVITY IN ACIDIC, BASIC OR ORGANIC ELECTROLYTE.
- RESISTANCE TO OXIDATION OR REDUCTION.
- SWELLING OR SHRINKAGE IN ELECTROLYTE.
- THERMAL STABILITY.

TABLE 1



FABRIC GEOMETRIC CHARACTERISTICS

- FABRIC THICKNESS.
- PORE SIZE AND SHAPE.
- UNIFORMITY OF PORE SIZE DISTRIBUTION.
- STRENGTH IN X AND Y DIRECTIONS.
- ELONGATION.

TABLE 2

1 by another speaker, of infinite length. These structures are
2 generally less uniform in thickness from point to point in
3 the fabric and in pore size. Strength is more nearly isotropic
4 in the X and Y directions, but this is usually not an important
5 factor in separator design.

6 The next slide shows how thickness may be built up
7 by superimposition of additional fibers -- next slide, please?

8 (Slide.)

9 And even given a strength in the Z direction by
10 mechanical entanglement of fibers down through the layers.

11 Next slide, please. (Slide.)

12 This shows a piece of textile machinery which is
13 used for making the random widths from staple fibers. Slide
14 off, please.

15 The next slide illustrates how plying of multi-layers
16 of oriented fibers can be used to build up increased thickness.
17 This serves to decrease the pore size by filling in some of
18 the slot-like spaces between individual fibers and increasing
19 the tortuosity of open pathways. (Slide.) Pore size can be
20 further decreased by compressing the fabric in the Z direction
21 which cuts down the interfiber space and thus the size of the
22 capillaries. I'll say more about this a little later.

23 Another technique which may be used to reduce the
24 pore size further is by mixing fibers of two or more diameters.
25 As can be seen in the next slide, I don't know if you can make

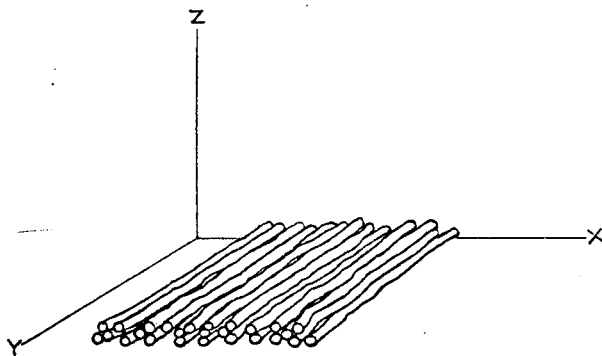


FIGURE 5

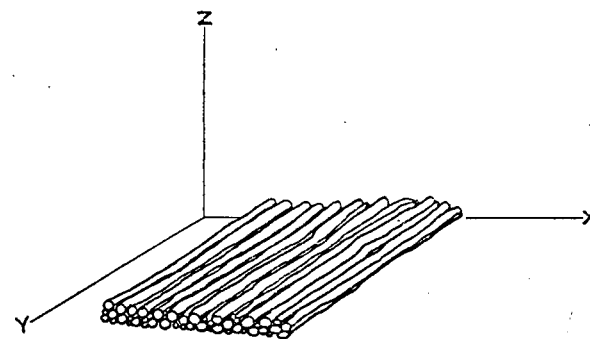
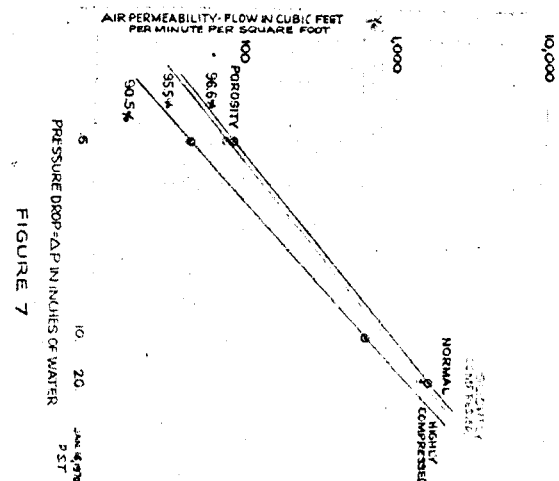


FIGURE 6

BINDER SYSTEMS

- HEAT AND PRESSURE - SELF BINDING.
- SOLVENTS.
- MECHANICAL ENTANGLEMENT.
- CHEMICAL ENTANGLEMENT.
- ADHESIVE BINDERS.

TABLE 3



EFFECT OF FABRIC COMPRESSION ON PERMEABILITY -
WEBRIL Nonwoven Fabric R2905

1 out the very fine fibers there -- but the small ones can be
2 used to fill in the voids between the large ones. (Slide.)

3 The next consideration is how to hold the fabric
4 together once the fibers have been laid out in the desired
5 manner. A number of choices is available here as shown in the
6 next slide. (Slide.)

7 This shows -- excuse me, I meant to introduce
8 this earlier -- this shows a number of machines which, each
9 of which has the capability of making a fibrous web of
10 parallel fibers and laying it, superimposing it on the previous
11 web on a continuous conveyer, so that we can build up
12 this multi-layered structure that I illustrated, and also
13 gives the capability of mixing the fibers of different diameters,
14 as I illustrated.

15 Next slide, please. (Slide.)

16 Now, back to binder systems. Heat and pressure may
17 be used with readily thermoplastic fibers, such as dynel,
18 polypropylene and cellulose acetate, but care must be taken to
19 avoid glazing over the surfaces and thus reducing permeability.
20 Solvents may be used with some thermoplastic fibers of high
21 melting point not susceptible to the pressure technique.
22 Chemical or mechanical entanglement may be used with cotton or
23 viscose rayon fibers which are not susceptible to heat or
24 solvent methods. Adhesive binders are commonly used in nonwoven
25 manufacture, but are not recommended for battery separators

rb-36

1 because they may decompose under oxidizing conditions and
2 make undesirable by-products that interfere with electrochemical
3 reactions.

4 Earlier I made some comments about the effects of
5 compression on pore size. The next slide illustrates (Slide)
6 how compression may be manipulated as a variable.

7 Mathematical expressions have been derived for the
8 estimation of pore size by the study of flow rates through
9 fabrics. Since this is much more convenient than other methods,
10 it has been adopted here to illustrate this point.

11 This figure shows plots of air permeability against
12 pressure drops for three variations in porosity of the same
13 material. The uppermost line shows one of our standard
14 cotton grades at its normal thickness, weight, and density.
15 The middle line shows the same material after it has been
16 calendered lightly; and the third line after calendering with
17 greater pressure.

18 The porosity shown on Figure 7 is calculated from
19 bulk density. The actual density of cotton fibers is very
20 close to 1.53, so that the porosity or fraction of voids can
21 be calculated from the known weight and thickness of the fabric
22 and its calculated density in relationship to the density of
23 cellulose in it. That is, the density of the fabric divided
24 by the density of cellulose gives the fraction of space
25 occupied by the cotton fibers and the rest of the volume is

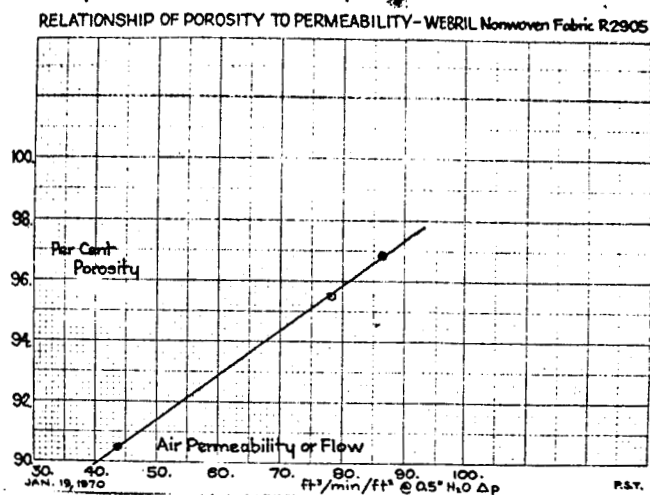


FIGURE 8

CAPACITY PARAMETERS

- WETTING ANGLE OF ELECTROLYTE ON FIBER POLYMER.
- FIBER DIAMETERS.
- PORE SIZE AS MODIFIED BY PRESSURE.
- FIBER FINISH ADDITIVE.

TABLE 4

TYPICAL STRUCTURES

| FIBER | BINDING SYSTEM | BATTERY END USE |
|---------------------|--------------------------------|---|
| Cotton | Chemical Entanglement | Mercury-Zinc Cuprous Chloride |
| Dynel | Mechanical Entanglement | Lead-Acid |
| Dynel | Heat and Pressure | Zinc-Air Lead-Acid Nickel-Cadmium |
| Polypropylene-Rayon | Apertured Linear Polypropylene | Zinc-Air |
| Polypropylene | Heat and Pressure | Nickel-Cadmium |
| Nylon | Solvent | Nickel-Cadmium Silver-Zinc |

TABLE 5

1 made up of voids.

2 Next slide. (Slide.) This shows a plot of air
3 permeability against porosity at a half-inch water drop
4 pressure across the fabric, one of a number of values that
5 could be considered. If we assume laminar flow and flow
6 pressure drop through the pores, we know that the rate of flow
7 is proportional to the fourth power of the dimension of the
8 pores measured normal to the direction of flow and inversely
9 proportional to the first power of the pore dimension in the
10 direction of flow. This brings us to a cubic function which
11 would plot as the straight line for flow rate, that is,
12 permeability versus porosity.

13 Even though we are not dealing with ideal cylin-
14 drical pores in the fabrics, but rather with slot-shaped pores
15 in the case of carded fabrics and rather oval-shaped pores in
16 the case of random fiber fabrics, the mathematics permit us
17 to use these plots as valid indicators or how we have delibera-
18 tely reduced pore size by application of external pressure to
19 these fabrics during their preparation.

20 Slide, please. (Slide.) When hydrophobic fibers
21 are chosen for their good resistance to oxidation and chemical
22 stability in electrolyte, a liquid capacity holding problem
23 is often encountered. The contributing factors are listed
24 in the next slide. (Slide.)

25 Wetting angle of electrolyte on the fiber polymer,

1 fiber diameters, pore size as modified by pressure, and fiber
2 finish additives. Slide off, please.

3 Unfortunately, wetting angle is difficult to
4 measure on individual fibers due to the narrow diameter of
5 textile fibers in general. It is usually measured on fabrics
6 or on films of polymers from which the fibers are made. An
7 excellent discussion of wetting and contact angle on various
8 substrates is found in Volume 43 of the the "Advances in
9 Chemistry" series published by the American Chemical Society
10 in 1964. It must be kept in mind, however, that wetting angles
11 of aqueous fluids on fibers or substrates are tremendously
12 affected by the finish the fiber producer applies to the
13 fiber. In most instances in fact the initial contact angles
14 measured on nonwovens are more dependent on fiber finish than
15 on the basic nature of the fiber polymer.

16 The additives which are present on hydrophobic fibers
17 and usually even on hydrophilic ones -- I'm talking about
18 staples, remember. These finishes are put on so they can be
19 handled on textile equipment and they may likewise give
20 objectionable products on oxidation and produce undesirable
21 electrochemical effects. Due cognizance should be taken of the
22 presence of these agents and their removal undertaken if
23 necessary. The same comment applies to fabric finishes
24 which may be applied after the fabric has been manufactured.

25 Typical separator structures which have been

1 designed and manufactured in commercial quantities for the
2 end uses shown are tabulated in the next slide.

3 (Slide.)

4 Cotton, particularly in the mercury-zinc primary
5 cells where the binder is absent-- It's actually a chemical
6 entanglement; it's also used in the cuprous chloride systems.
7 Dynel by mechanical entanglement, binder systems in lead-acid.
8 Dynel by heat and pressure system, in zinc-air, lead-acid,
9 and nickel-cadmium.

10 Polypropylene-rayon mixtures held together by an
11 apertured film made of linear polypropylene in zinc-air
12 system. Polypropylene fiber put together with heat and
13 pressure in nickel-cadmium; and nylon held together by a
14 system which is proprietary I understand, and used in nickel-
15 cadmium and silver-zinc.

16 Most of the structures may be used as separators or
17 absorbers without further treatment. In the case of fabrics
18 made from polypropylene fiber, absorption qualities or capa-
19 bilities can be improved by irradiation techniques.

20 Now, when penetration by very fine dendrites must
21 be prevented, or control or gaseous diffusion undertaken,
22 these structures may serve as scaffolding for deposit or other
23 membrane materials or be put in laminated structures where
24 the necessary control is achieved through an additional layer,
25 such as a semiporous membrane.

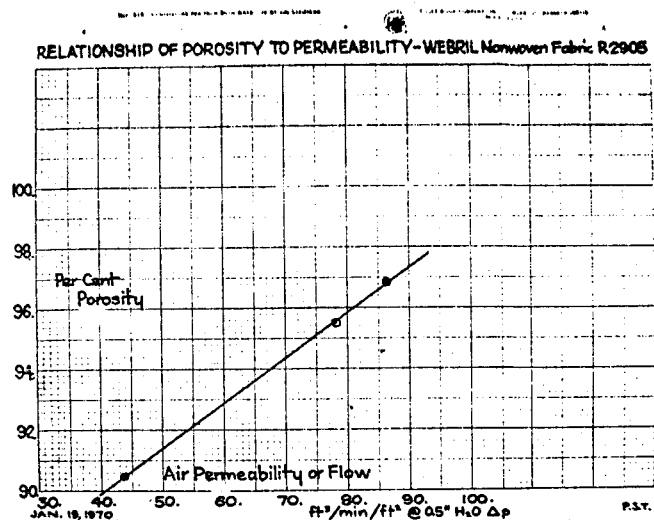


FIGURE 8

CAPACITY PARAMETERS

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| Nylon | Solvent | Nickel-Cadmium Silver-Zinc |

TABLE 5

1 Now what I have tried to talke about here today has
2 been the opportunities available for the choice of fiber,
3 fiber manipulation and fabric unification systems to achieve
4 desired ends. But, there are two major difficulties encountered
5 in the design of nonwoven fabrics for battery separators.

6 One is that textile labs, manufactuers, are rarely
7 if every equipped to run electrochemical testing of proposed
8 separator materials, and therefore, these tests must be run
9 in the laboratories of the battery manufacturers.

10 The other problem is -- and this is the really big
11 one -- is the one of identifying what is required. To
12 overcome these difficulties, the nonwoven producer and the
13 battery manufacturer must establish better communication at
14 the technical level so that the fabric design skills may be
15 directed in a most efficient manner.

16 Mounting a joint effort to define requirements and
17 them employing nonwoven manufacturing techniques to achieve
18 them presents some obstacles, but certainly they are surmoun-
19 table ones..

20 Thank you.

21 (Applause.)

22 If you have any questions, I will try to answer
23 them.

24 HENNIGAN: I think we'll take about a 10 minute --
25 oh, we have one question here.

|rbQ.41.

1 CARR: Bill Carr, Eagle Picher.

2 I just have one question regarding the way you might
3 manufacture a nonwoven material. This contrasting two of your
4 materials, for example, E1451 polypropylene by comparing it
5 to something like EM490. In appearance they are nothing at
6 all alike.

7 DANGEL: Yes.

8 CARR: One is very slick and the other is very
9 permeable, I guess.

10 Can you maybe explain a little bit the differences
11 as per your discussion?

12 DANGEL: Yes. The first number, E1451 is 100
13 percent polypropylene. The other one was half-nylon and
14 and half-polypropylene, the EM490. These were both unified
15 by the heat and pressure technique. The effect of having
16 the nylon present on the surface in 50 percent proportion
17 prevented a glazing over of this surface by the heat and
18 pressure with which this fabric was unified.

19 CARR: Based on what we know, it seems that the
20 glazing over of the surface is undesirable.

21 DANGEL: Yes. This is something we are aware of
22 and are working to ameliorate.

23 Thank you.

24 HENNIGAN: Are there any further questions for
25 Mr. Dangel?

1 We will take a ten-minute coffee break.

2 (Recess.)

3 HENNIGAN: Our next speaker this morning on
4 separators, to do mainly with the OAO battery, is Steve
5 Gaston from Grumman Aircraft.

6 STEPHEN GASTON: In this presentation the organic
7 and inorganic impurities of the Pellon material used for
8 the OAO cell and the dynel and the viskon materials used
9 during the formation of the OAO cell will be presented.

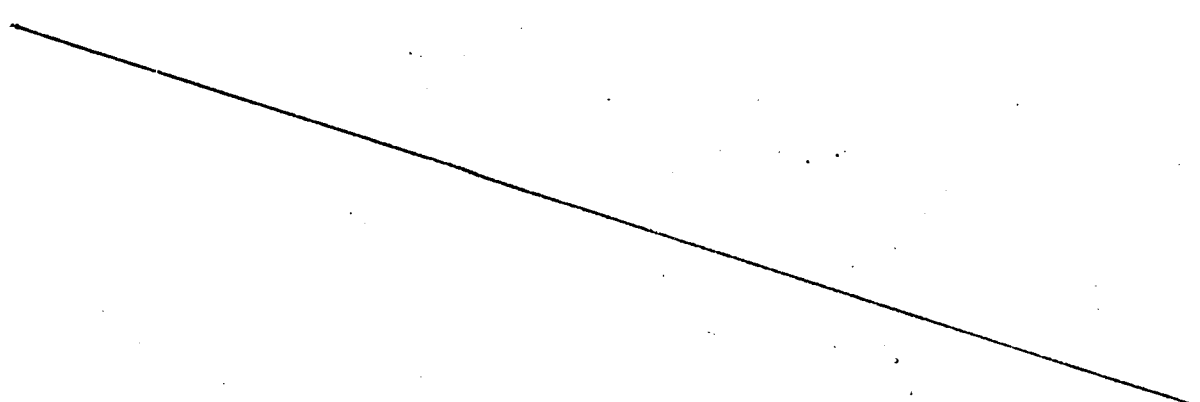
10 Other physical properties, such as thickness
11 variations, electrolyte absorption, resistance, tensile
12 strength, et cetera, were also examined.

13 However, a more thorough evaluation of the
14 techniques applied and data obtained is required and
15 it will be reported at a future date.

16 On Table 1 -- which I have shown here --

17 (Slide.)

18 I have to make a few corrections. On the maximum values there
19 only should be three significant figures; so the last number
20 should have been crossed out. The percent chloride content
21
22
23
24
25



1 in the minimum value column, it should be 0.28 not .028.

2 Essentially what we have shown here is the separator
3 loss which we have used for four OAO batteries. For three
4 batteries we have used Pellon Lot No. 16015. The the last OAO
5 battery we used Lot No. 17160.

6 I believe there is another correction. I believe
7 the designation ML has been removed by Pellon. Maybe Pellon
8 would like to comment on it. The same basic style as we had
9 used previously is being applied.

10 For the organic content determine the procedure
11 specified in the interim cell specification was used.
12 Essentially it consists of the following steps.

13 First, each of the three samples was cut to 10 cm
14 square and weighed on an analytical bance.

15 Second, the sample was inserted into a weighted
16 container with the specific quantity of reagent grade methanol
17 and magnetically stirred overnight.

18 The sample was removed and weighed after drying.
19 Solvent was filtered, evaporated, and brought to constant weight.

20 A thin film of each residue was placed between
21 sodium chloride crystals and inserted into a Perkin-Elmer
22 model 21 infrared spectrophotometer for spectral scanning from
23 2 to 15 microns.

24 I should note here in some instances, a larger
25 sample -- double in size -- was required to get a readable

1 spectrum.

2 The results show variations in the organic contents
3 between the three samples from each lot. Shown in this table
4 are the minimum and maximum values. Also differences between
5 the two lots can be noted.

6 The last column designated as maximum value shows
7 the highest value obtained between the samples of the two lots.
8 A number of different values for the percent weight loss for
9 Lot No. 16015 was obtained. And also it should be noted that
10 in addition to the use of different solvent materials, the
11 ethanol and methylene chloride results were reported by ESB
12 in their fifth quarterly report on alkaline separator studies
13 for NASA-Goddard Contract NAS 5-10418, dated June - September,
14 1968.

15 The percent loss by the methanol technique was
16 reported by U.S. Testing Company, Hoboken, New Jersey. There
17 appears to be a closer correlation between the methanol and
18 the methylene chloride extractions than the ethanol and the
19 methylene chloride extractions. The specification target of
20 two percent was slightly exceeded in Lot 16015, but was met in
21 the later lot. It still seems reasonable that the maximum
22 target of two percent should be kept in the specification.

23 The inorganic content determination method was as
24 follows:

25 Each of these three samples was cut to 10 cm square

1 and extracted using water. It was found that more than one
2 sample was required to get a workable amount of residue.
3 Specifically, two samples were required.

4 A quantitative analysis for nitrate, silicon,
5 carbonate, nickel, zinc, titanium and chloride were conducted
6 using the following methods:

7 For the nitrate, the Taylor method with phenoldi-
8 sulfonic acid.

9 The silica, the Taylor method using color reagent
10 one and two.

11 The carbonate-barium chloride method.

12 For the nickel, atomic absorption method.

13 For the zinc, the atomic absorption method.

14 For the titanium, the sulfuric acid peroxide
15 colorimetric method.

16 And for the chloride, the Mohr method.

17 The emission spectrograph analysis were conducted
18 on extracts that were ashed and then analyzed for inorganic
19 constituents using a Baird atomic emission spectrograph..

20 The total maximum inorganic content was 0.25 percent
21 which is also the maximum target value specified both in the
22 interim cell specification and the Grumman OAO cell specification.

23 (Slide.)

24 On Table 2, the separator analysis for the viscon
25 material used is shown. I don't have at the moment the viscon

1 part number. I have a receipt number. I don't have at the
2 moment a specific viscon lot number. It's available and I
3 think I can get it at a later date.

4 Essentially a combination of viscon and dynel
5 is used for the chemical cleaning or plate formation
6 process. That's one of the reasons why we analyzed -- had
7 the viscon and the dynel analyzed. The total organic and
8 inorganic content for the viscon material is comparable to the
9 results for the Pellon material analysis. I would say it's
10 slightly lower for the zinc and for the chloride.

11 The third graph (Slide) shows the analysis for
12 the dynel material. And again, it can be noted this is less
13 variation for the Pellon and viscon materials -- no, correction,
14 I'll take that back. In the dynel there is less variation in
15 the results than shown, than observed for the viscon and Pellon
16 materials. Therefore the maximum values are lower.

17 Table No. 4 (Slide) shows a -- this is redrawn from
18 a spectrogram -- for separator lot number 17160, which is the
19 last one used, and it shows absorptions which may be
20 characterized as follows:

21 The presence of the N-H absorption is indicated
22 in the 3 to 3.05 micron range and the C-H in the 3.4 to 3.5
23 range.

24 The $C=O$ frequency appears in the 5.8 to 5.85 range
25 as expected for the $C=O$ group.

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DAO PELLON SEPARATOR ANALYSIS

| o APPLICABLE BATTERY | S/N 25A, 26A, 30, 31, 32, 33 | S/N 34, 35 | MAX VALUE |
|----------------------|------------------------------|---------------|-----------|
| o PELLON STYLE NO. | 2505 ML | 2505 ML | |
| - LOT NO. | 16015 | 17160 | |
| o ORGANIC CONTENT | | | |
| - % RESIDUAL | 1.27 - 2.44 | 1.35 - 1.50 | 2.44 |
| - % WT. LOSS: | | | |
| METHANOL | 2.50 - 2.58 | 1.23 - 1.29 | 2.58 |
| ETHANOL (ESB) | 0.60 - 0.80 | | 0.80 |
| METHYLENE CL (ESB) | 1.20 - 2.00 | | 2.00 |
| o INORGANIC CONTENT | | | |
| - % ASH | 0.111 - 0.170 | 0.180 - 0.250 | 0.250 |
| - % NITRATE | 0.00012 - 0.00015 | 0.032 - 0.038 | 0.038 |
| - % SILICA | N/D | 0.044 - 0.045 | 0.045 |
| - % CARBONATE | 0.650 - 1.120 | <0.003 | 1.120 |
| - % NICKEL | N/D | 0.010 - 0.011 | 0.011 |
| - % ZINC | N/D | 0.160 - 0.200 | 0.200 |
| - % TITANIUM | N/D | ≤ 0.008 | 0.008 |
| - % CHLORIDE | 0.062 - 0.130 | 0.200 - 0.280 | 0.280 |

- o SPECIFICATION TARGET - LESS THAN 2.0% BY WEIGHT TOTAL ORGANICS
- LESS THAN 0.25% BY WEIGHT TOTAL INORGANICS

DAO CELL FORMATION SEPARATOR ANALYSIS - VISCON

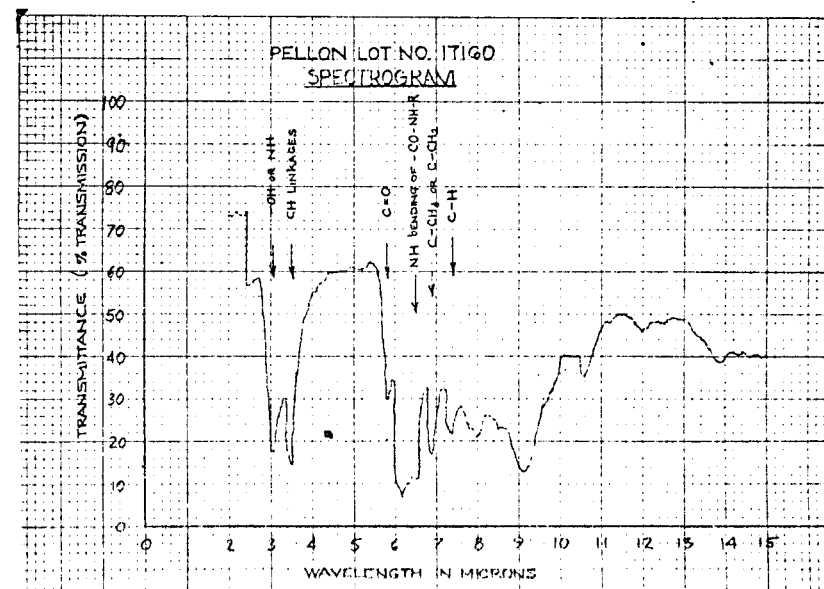
| o APPLICABLE BATTERY | S/N 25A, 26A, 30, 31, 32, 33 | S/N 34, 35 | MAX VALUE |
|----------------------|------------------------------|---------------|-----------|
| o VISCON P/N | 8787 | 8787 | |
| o ORGANIC CONTENT | | | |
| - % RESIDUE | 0.290 - 2.330 | 0.510 - 0.700 | 2.330 |
| - % WEIGHT LOSS | 1.340 - 1.910 | 0.570 - 0.670 | 1.910 |
| o INORGANIC CONTENT | | | |
| - % ASH | 0.049 - 0.204 | 0.065 - 0.130 | 0.204 |
| - % NITRATE | 0.00010 - 0.00012 | 0.029 - 0.050 | 0.050 |
| - % SILICA | N/D | ≤ 0.018 | 0.018 |
| - % CARBONATE | 0.539 - 0.631 | 0.005 - 0.018 | 0.631 |
| - % NICKEL | N/D | ≤ 0.010 | 0.010 |
| - % ZINC | N/D | ≤ 0.003 | 0.003 |
| - % TITANIUM | N/D | ≤ 0.004 | 0.004 |
| - % CHLORIDE | 0.048 - 0.110 | ≤ 0.060 | 0.110 |

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DAO CELL FORMATION SEPARATOR ANALYSIS - DYNEL

| o APPLICABLE BATTERY | S/N 25A, 26A, 30, 31, 32, 33 | S/N 34, 35 | MAX VALUE |
|----------------------|------------------------------|---------------|-----------|
| o DYNEL P/N | 7354 | 7354 | |
| - R.R. NO. | | | |
| o ORGANIC CONTENT | | | |
| - % RESIDUE | 0.270 - 1.520 | 0.570 - 0.760 | 1.520 |
| - % WEIGHT LOSS | 1.000 - 1.400 | 0.660 - 0.780 | 1.400 |
| o INORGANIC CONTENT | | | |
| - % ASH | 0.021 - 0.122 | 0.023 - 0.044 | 0.122 |
| - % NITRATE | 0.00011 - 0.00093 | 0.019 - 0.026 | 0.026 |
| - % SILICA | N/D | ≤ 0.015 | 0.015 |
| - % CARBONATE | 0.484 - 1.191 | <0.004 | 1.191 |
| - % NICKEL | N/D | <0.010 | 0.010 |
| - % ZINC | N/D | ≤ 0.003 | 0.003 |
| - % TITANIUM | N/D | ≤ 0.004 | 0.004 |
| - % CHLORIDE | 0.042 - 0.101 | 0.110 - 0.130 | 0.130 |

GRUMMAN



rb-48

1 The band near 6.5 microns is indicative of N-H
2 bending of the -CO-NH-R.

3 The 6.9 micron range is indicative of the -C-CH₃
4 of the C-CH .

5 The 7.3 to 7.4 micron range is indicative of the C-H²
6 presence.

7 And in general it appears that the spectra is
8 similar to Sadtler's Standard Spectra for a complex Fattyamine.

9 That's all I have.

10 (Applause.)

11 HENNIGAN: Do we have any further questions on the
12 separators for the OAO batteries?

13 FORD: Ford, NASA Goddard. Steve, I believe, and
14 correct me if I am wrong, that the point of .25 percent on the
15 inorganic has been changed. It's no longer a target when you
16 put it at one percent maximum, is that correct?

17 GASTON: Yes, at one time we did change it to one
18 percent. We have one additional separator which I haven't
19 mentioned. That is the separator for the auxiliary electrode
20 cell. And that was somewhat higher.

21 However, looking at the results in the last separator
22 lot, I think we can change the target specification back to
23 quarter percent inorganic content rather than keep that one
24 percent. Essentially what I say somewhere in the past we did
25 have a high result and therefore we did change the specification.

1 We would like to change it back to quarter percent.

2 HENNIGAN: The next speaker will be myself on some
3 of the information that we have gotten on polypropylene
4 separators and we do have some comparison with nylon.

5 Now most of these -- well, all of these materials
6 were selected in the program at Electric Storage Battery
7 Company, Norberg Research Center, and the selected materials
8 were delivered to Eagle Picher, who built these materials into
9 six ampere cells, the regular steel, ceramic sealed cells.
10 These cells do have Schlage locks on them so we can put
11 guages or make gas analysis later on if we want to.

12 There is another thing we are trying to do here. I
13 don't know if we have been too successful. We do have some
14 numbers. But again, what do these numbers mean? We make
15 these wicking tests and wetting tests and absorption tests and
16 so forth and can we pick out a good separator from these
17 numbers? And I'm not saying we can. I'm just going to show
18 you the data and you will have to decide for yourself.

19 There's a lot more data on these things. I think
20 if we tried to put it all up here we would inundate you with
21 it. I tried to pick out the data that normally people use
22 in looking at a separator for a cell.

23 I wonder if I could have the first slide. (Slide.)

24 This separator here is a Kendall material and it's
25 polypropylene.

1 Now all of these slides will have the control
2 separator in the bottom or near the bottom slot. And on the
3 left here we have the separator designated as E1451. AR
4 throughout this talk will mean as received, as to materials
5 delivered. W means washed out. And I will discuss that in a
6 few minutes. T means treated.

7 Our graph here shows the ampere hours to one volt at
8 a six amp discharge. Now this is the C rate for the cell.
9 Now this material here had somewhat of a higher resistance
10 than normally we see but we wanted to build some cells out of it
11 to see how much resistance did affect this. And the as
12 received material did have a resistance of 34 ohm cm. It
13 also had a very low air permeability. Wetting time was not
14 too bad. Wicking would look attractive to most people. And
15 the absorption was considered to be low here.

16 However, at the C rate, we only got 3.2 ampere hours
17 out and the charge voltages were about 150 and pressure build
18 up in the cell was 30 pounds psi guage. We tried washing this
19 material out. I think this was washed in methanol, then dried.
20 The resistance went up by a factor of three. Wetting time --
21 it just wouldn't wet. And Wicking was approximately zero.
22 And we still got about the same number of ampere hours.

23 The treated material was washed out, as I mentioned
24 before, but it was treated with concentrated sulfuric acid
25 to see if it could improve the wetting properties of the surface.

1 Of course, it was washed out after the acid treatment within
2 about 10 times or more in deionized water.

3 We didn't do much to improve the wicking here.
4 We did decrease the resistance again, and wetting time was
5 improved. Air permeability in all three cases stayed about
6 the same. There was some improvement here in the ampere hours
7 in the C rate.

8 Our control material is the 2505 Pellon material,
9 hot calendered as received. This has what is considered to be
10 somewhat of a low wicking. It has a very good KOH absorption.
11 The resistance is low. The wetting time is not considered too
12 bad. And air permeability here was 61, which is quite high.

13 Now the cells, we got 6.1 ampere hours and I forgot
14 to point out the voltages up above there, but there were still
15 rather high in the Kendall materials. The Pellon material of
16 course was I'd say normal and the pressure was seven.

17 I might mention that all these charges are to C over
18 10 for about 16 hours.

19 Can we have the next slide please. (Slide.)

20 These separators here, the first one FT2140 is a
21 Pellon polypropylene. We again have the 2505K4 which is
22 the Pellon material. And a material that was given to us by
23 Hercules. I don't know really of a number of this material.
24 It's made by a fellow, Dr. Burroughs at the Research Triangle
25 in North Carolina. You have to trace that one down.

1 But the Pellon material here, wicking was just --
2 wouldn't wick. And KOH absorption was, well, we'd call that
3 fair. AC resistance low. Wetting time seemed to be quite
4 long. And air perm was I guess reasonable.

5 This one gave us 6 ampere hours at the C rate. The
6 voltage was 1.45 and the pressure went up to about 12 at the
7 end of charge.

8 The Pellon material here, the K4, was washed out
9 in dilute hydrochloric acid and the properties, well it didn't
10 change too much, but I guess the air perm went up a little bit.
11 This dropped the ampere hours to 5.5 and the voltage was slightly
12 lowered. Pressure about the same.

13 The control material is given here again. This
14 will be shown on the next slide for comparison.

15 Now the Hercules material at the C rate gave us
16 4.8 ampere hours. Fairly low voltage, the C over 10 and the
17 pressure went up to 26. Now the exact material that was used in
18 here we don't have the data yet from the ESB but from some of
19 the information I got from Eagle Picher it looks like the
20 KOH absorption is about 10. And this material wicks very fast.
21 And if you put it in KOH it just -- it's a very fast wicking
22 material. I don't have any idea of the AC resistance.
23 Wetting time is very fast. I would say on the order of less
24 than a minute. And we don't have any information yet on the
25 air perm.

1 Next slide, now, please. (Slide.)

2 This separator WX1242 is made by the GAF Corpora-
3 tion, General Aniline Film. This is a polypropylene, also.
4 There are the numbers for the wicking. Air permeability is
5 quite high on these materials. Wetting time is reasonable.
6 AC resistance is low. We got six ampere hours at the C rate on
7 the as received material. The under charge voltage was 1.45 and
8 pressure was about 18.

9 This material was also washed out in methanol and
10 then washed in water, deionized water, so here we change one
11 of the properties considerably -- the wetting time. And we up
12 the air perm a little bit. But it just correlates beautifully
13 here, the ampere hours is higher now and the pressure stayed
14 about the same in the under charge voltage stayed about the
15 same.

16
17 And the latter is the Pellon control as received
18 which is shown on the slide before.

19 All this information so far is at the C rate.
20 There is a little stress on the cell. We normally don't use
21 them at these rates. We do have some comparative data for C
22 over 2.

23 Can I have the next slide, please.

24 (Slide!)

25 That shouldn't be C-plus, it should be C and C

SEPARATOR E1451

| | WICKING cm. in 5 hr. | KOH ABSORPTION g cc. dry vol | AC RESISTANCE ohm-cm. | WETTING TIME minutes | AIR PERM. cc./sec. | |
|-------------------------|------------------------------|---------------------------------|-----------------------------|-------------------------|-----------------------|-----|
| E1451 AR | EOC=1.50 3.2 P=30 | 6.6 | 1.4 | 34 | 14 | 1.8 |
| E1451 W | EOC=1.50 2.9 P=20 | 0 | 0.7 | 96 | >1440 | 1.7 |
| E1451 T | EOC=1.48 4.8 P. | 0.1 | 0.7 | 32 | 81 | 1.7 |
| CONTROL 2505K4 AR | EOC=1.43 6.1 P=7 30 60 | 1.0 | 3.1 | 2.8 | 11 | 61 |

AMPERE HOURS TO 1.0 V
AT 6.0 AMPERE
DISCHARGE

EOC=END OF CHARGE
VOLTAGE
P=PSIG

SEPARATORS FT2140, 2505K4 + HERCULES

| | WICKING cm. in .5 hr. | KOH ABSORPTION g./cc. dry vol. | AC RESISTANCE ohm-cm. | WETTING TIME minutes | AIR PERM. cc./sec. | |
|-------------------------|--------------------------|-----------------------------------|-----------------------------|-------------------------|-----------------------|----|
| FT2140 | EOC=1.45 6.0 P=12 | 0 | 2.8 | 1.7 | 45 | 51 |
| 2505K4 W | EOC=1.43 5.5 P=12 | 0.1 | 3.5 | 2.1 | 57 | 79 |
| CONTROL 2505K4 AR | EOC=1.43 6.1 P=7 | 1.0 | 3.1 | 2.8 | 11 | 61 |
| HERCULES | EOC=1.44 4.8 P=26 | | | | | |
| | 3.0 6.0 | | | | | |

AMPERE HOURS TO 1.0 V
AT 6.0 AMPERE
DISCHARGE

EOC=END OF CHARGE
VOLTAGE
P=PSIG

SEPARATOR WEX 1242

| | WICKING cm. in 5 hr | KOH ABSORPTION g/cc. dry vol. | AC RESISTANCE ohm-cm. | WETTING TIME minutes | AIR PERM cc./sec. | |
|-------------------------|------------------------------|----------------------------------|-----------------------------|-------------------------|----------------------|-----|
| WEX1242 AR | EOC=1.45 6.0 P=18 | 0.3 | 2.4 | 3.2 | 14 | 96 |
| WEX1242 W | EOC=1.45 6.5 P=15 | 0 | 1.4 | 2.9 | >1440 | 125 |
| CONTROL 2505K4 AR | EOC=1.43 6.1 P=7 30 60 | 1.0 | 3.1 | 2.8 | 11 | 61 |

AMPERE HOURS TO 1.0 V
AT 6.0 AMPERE
DISCHARGE

EOC=END OF CHARGE
VOLTAGE
P=PSIG

COMPARISON OF CAPACITIES AT C+C/2 RATES
C=6 AH

| SEPARATOR | CAPACITY AT C RATE TO 1.0 VOLT | CAPACITY AT C/2 RATE TO 1.0 VOLT |
|-----------|-----------------------------------|-------------------------------------|
| E1451AR | 3.2 | 4.7-6.2 |
| E1451W | 2.9 | 5.3-6.2 |
| E1451T | 4.8 | 6.5 |
| WEX1242AR | 6.0 | 7.5 |
| WEX1242W | 6.5 | 7.6 |
| FT2140 | 6.0 | 7.4 |
| 2505K4W | 5.5 | 7.5 |
| HERCULES | 4.8 | 7.3 |
| 2505K4AR | 6.1 | 7.3 |
| (CONTROL) | | |

1 over 2 rates. Again C equals six ampere hours.

2 The separator numbers are listed in the first
3 column. Capacity at C rate which was on the graphs before is
4 listed in the second column. In the third column you get C over
5 2 capacity.

6
7 The first three materials I previously mentioned
8 are the Kendall materials as received, washed out and treated.

9 The reason I gave a range on the first two there
10 was there was quite a range in capacities, I guess I forgot
11 to mention before this is always a sample of six cells we are
12 talking about. And the rest of them were a tenth or two
13 tenths of an ampere hour. The 1242 material again is the
14 General Analine Film. The FT2140 is Pellon. The 2505K4 is
15 Pellon. And Hercules material as mentioned before.

16 Now it looks here a couple of these Pellon materials
17 look very comparable to the operation with the nylon separator.
18 Of course, we are only talking about a couple of cycles here.
19 How this material is going to hold up in a cycling program is
20 the big question.

21 What we plan to do with these cells is cycle them
22 at Crane and about every three months we will pull one and
23 bring it back to Goddard here and compare the properties of the
24 material with the virgin samples. In the meantime we might
25 get some better tests for the wetting properties and absorption

1 properties and so forth.

2 Thank you.

3 (Applause.)

4 Are there any questions, please. Cohn?

5 COHN: Cohn, NASA.

6 I noticed that on your initial four or five slides,
7 something like that you had quite a few different physical
8 properties which as far as I could see didn't really correlate
9 with anything that we are after. I wonder whether you could
10 make a decision now by hindsight whether some of these
11 properties perhaps need not be determined because they don't
12 have any influence and whether perhaps there are other
13 properties that you may have found out about meanwhile that
14 could be more useful that should be measured, which have been
15 measured, so far.

16 HENNIGAN: Well, we hope to go back to, by hindsight,
17 to find out how these properties are changing with time.

18 Now there were some other properties -- quite a
19 few other properties we measures that I just couldn't see any,
20 there wasn't much correlation here except as I say on resistance;
21 there was one that gave you an indication that 30 ohm cm is
22 too high.

23 But as far as -- these are the type of tests people
24 are normally using. I'm trying to show you they aren't very
25 good to pick out the separator that we need. I am just

1 emphasizing the point here that has been mentioned three or
2 four times already: We don't have any information to give
3 the fiber manufacturer to really tell us where we got a good
4 separator for a battery. It's very surprising some of these
5 materials won't wick at all yet they work well in cells and
6 normally you would throw some of these materials out long ago.

7 Wil Scott, of TRW?

8 SCOTT: I gathered that wicking tests were done in
9 air at atmospheric pressure, is that correct?

10 HENNIGAN: That's right,

11 SCOTT: Has any comparison been done with the
12 wicking rates in a vacuum?

13 HENNIGAN: Well, they've done it in the presence
14 of nitrogen. I didn't see any effects there. Not in vacuum.
15 I haven't done anything in vacuum.

16 SCOTT: One other question.

17 I notice you used calendered Pellon, 2505, as a
18 control. And the maximum loft material has been used mostly
19 in other cells. Why was the K, calendered material used in
20 this case?

21 HENNIGAN: One of the reasons is we are having an
22 awful lot of trouble getting any control on the thickness of
23 maximum loft. It's difficult to handle the cells. We did
24 use the K4 to also look at a new Pellon material here.

25 Eventually we expect to go back and get some more cells and

1 include maximum loft in the next set.

2 BILLERBECK: Billerbeck, COMSAT.

3 Tom, I wanted to ask if there was any accelerated
4 testing of the separator in this program like boiling hot
5 KOH or any sort of accelerated test, relative test, of the
6 separators.

7 HENNIGAN: There was some tests, tensile strength
8 test on that high temperature, and there was also some, I
9 don't know what you call accelerated -- see, we are also
10 interested in some of these materials for silver cells and
11 there was also some tests done with silver oxide.

12 I got some information on that. It's a little bit --
13 some of the materials lost weight; some of them gained weight.
14 Some of them picked up silver actually in this test. And it's
15 kind of normal for the nylons to pick up silver.

16 BILLERBECK: Yes. Well, we've been wondering if
17 there is any good accelerated test that one can use for
18 looking at separator degradation. I just wondered if you had
19 any comments on that stemming out of this program.

20 HENNIGAN: Well, on the silver oxide test, for
21 instance, the Kendall materials gained some weight. The GAF
22 materials, well, it depended on whether you as-received it
23 or washed it. In the first case it lost and in the second
24 case it gained. And then in the rest of the materials, it's
25 about a five to 10 percent loss. But I don't know if there is

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1 any correlation with cell testing in this information either.

2 Bob Corbett?

3 CORBETT: I wonder as far as the capacity data at the
4 C rate, I guess these cell capacities were all measured at the
5 same point, as they went through the same previous history and
6 all that?

7 HENNIGAN: That's right.

8 CORBETT: And what was the electrolyte quantity
9 comparison between cells? Was it the same amount or was it
10 optimized for that separator?

11 HENNIGAN: No, it was optimized for each separator.
12 Now we did -- one of the reasons we put Swageloks on them,
13 we -- some of these cells that are low, one of the things I
14 think I'll do is try to start adding electrolyte to these cells,
15 maybe we didn't add enough.

16 CORBETT: So these were starved cells, so-called?

17 HENNIGAN: Yes.

18 CORBETT: Okay.

19 HENNIGAN: Regular sealed Ni-cad cells. You would
20 call them space type. Mr. Dangel?

21 MR. DANGEL: Is there any correlation between
22 thickness of the separator and the capacity of the cell?

23 HENNIGAN: The Kendall materials were about half the
24 thickness of all the rest. And I think the Kendalls were five
25 times ten to the minus three cm, and the rest were about ten or 12.

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1 DANGEL: Is this an indicator of anything that we
2 should be doing that could be useful? If we improved the
3 thickness would that give you better capacity?

4 HENNIGAN: Well, that cell there had the lowest
5 amount of electrolyte in it because it has the least amount
6 of separator. I'd say if we had a thicker separator and we
7 treated this with the sulfuric acid, we might be successful
8 there. As you know, if the seal were too great, that cell did
9 come up in capacity to a fairly decent number six and a half.
10 And it looked like it needed something done to it. And the
11 sulfuric acid treatment seemed to help.

12 COHN: Cohn, NASA, again. Stimulated by Billerbeck's
13 question, I'm just wondering whether perhaps Dr. Wieninger's
14 triangular sweep might be applied in this case as a method of
15 getting cadmium into or silver for that matter into or near
16 the separator and finding out how the separator stands up.
17 Perhaps Dr. Wieninger would care to comment on the possibility
18 of using this as an accelerated test method of separators.

19 WEININGER: Weininger, GE.

20 I really have to think about that a little bit.
21 But the point of the method is that you are always under
22 potential static control. And just thinking off the top of my
23 head I would say that it, the migration would be reduced if
24 you do not allow the peak of the triangular sweep to go to
25 high voltage. However, if you do so on purpose, then you

1 are going to run into very heavy oxygen evolution at the
2 positive electrodes, and surely you could in a very short time
3 also oxidize your cadmium and get it into the separator.

4 Is that the question?

5 COHN: Yes.

6 WEININGER: Offhand, I don't see any reason why
7 you couldn't do that very rapidly, yes.

8 HENNIGAN: John Leuthard?

9 LEUTHARD: Leuthard, Martin Marietta.

10 Tom would I be right in assuming that if on some
11 particular cell the material parameters are established for
12 a particular cell and that cell subsequently operates satis-
13 factorily, that these parameters could be used to inspect
14 subsequent lots of material that is bought and would all these
15 parameters be applicable?

16 HENNIGAN: Like if we picked one like the Pellon
17 material?

18 LEUTHARD: Right. If you took say 2140 and we
19 established these parameters to be whatever you had up there
20 or whatever the material we bought at that time, and those
21 cells were built from that material operated satisfactorily,
22 then could that same set of parameters be used for subsequent
23 lot buying of the particular type of separator?

24 HENNIGAN: Well, we only have one lot here. I
25 don't know how they can vary lot to lot. Now in Pellon

1 materials, the nylon that we normally use, I think we get quite
2 a bit of variation in that lot to lot. There's no -- we try
3 to hold say that organic content down to less than two
4 percent but as you see in the OAO battery some of it was
5 up a little higher than two percent. If you are in production
6 do you hold because it's 2.4 or go get another lot? That is
7 the question. And it's -- I don't know how good these parameters
8 are lot to lot, no.

9 LEUTHARD: Do you know whether some parameters are
10 more significant than others with respect to that kind of
11 inspection criteria?

12 HENNIGAN: The only one there that looked like
13 there was a high resistance correlating with the low capacity
14 -- as far as a good feel for this thing, the Hercules
15 material looked like it would be a terrific separator. It
16 absorbed quite a bit of electrolyte. I didn't have any numbers
17 on that. Wicked very well and so forth. At the C rate it
18 didn't operate well, when we put it down to C over 2 it
19 worked fine. So maybe some of these, depending on what you
20 want to use the cell for --

21 LEUTHARD: Well, we're interested right now for
22 heat sterilizable separator material for the Viking cells,
23 nickel cad, and we are looking at polypropylene because
24 the nylons just won't stand the high temperatures.

1 wicking and so we are interested -- anybody that has any
2 information, we would certainly be grateful.

3 HENNIGAN: Dr. Will, of General Electric?

4 WILL: The difference in end capacities seem to
5 amount to as much as a factor of two. Now that is really
6 quite a terrific discrepancy in these test results. Now assume
7 of course that the conditions that you had in hand like the
8 thickness of the plates, the free volume in sealed cells was
9 exactly the same all of these cells, and the question is
10 unescapable since there was no trend, no systematic trend to
11 be observed in any of the parameters studied, the question
12 is unescapable as to which property indeed then causes this
13 surprising discrepancy of a factor of two.

14 Now, is there some standardization missing? Is
15 there need for looking at precisely the same thickness of the
16 separator? Do we know enough about the porosity, the different
17 porosities of these various separators?

18 It seems to me that the amount of electrolyte
19 contained in the battery might be the major parameter
20 involved here that might account for the large discrepancies of
21 a factor of two.

22 HENNIGAN: Well, that's one of the reasons we put
23 the Swageloks on there so we can add more electrolyte.
24 Of course it's very difficult to take any out once you spin
25 them but you can measure that amount, but we would like to add

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1 more to those cells that were very low.

2 Earl Carr?

3 CARR: I'd like just to say one thing. With
4 respect to the capacity of the cells at the two different rates,
5 definitely do have a trend and that the internal or the
6 AC resistance measurement of the separator is definitely
7 correlated with loss of performance.

8 I might also just add that even though the El451
9 materials were the thinnest, they have the highest resistance.
10 Of course, we are talking to Mr. Dangel about that. The
11 surface is a glazed surface and it seems to give some
12 difficulty as far as permeability. I think the two are
13 related.

14 Those cells were shimmed using stainless steel
15 shims on each end of the cell case to maintain the same
16 approximate impression on the stack or in the cell core.
17 Based on the free volume calculations and the adjustments of
18 electrolyte we feel that they are quite equal, at least as close
19 as we can come.

20 LACKNER: Lackner, DRE, Canada.

21 There is a factor that's possibly missing here.
22 I think they are mentioning electrolytes. In your washing
23 in your sulfuric acid treatment, it seems to me that you have
24 a higher resistance and you had a lower wicking rate.

Now, is it possible that the wetting agent which

1 has been mentioned has been washed out because all of these
2 materials are hydrophobic anyway, without the wetting agent,
3 we are not getting as much electrolyte in the separator as
4 we should. And so we are creating a higher resistance and
5 our lower capacities.

6 HENNIGAN: Well, the as-received had AC resistance,
7 you are talking about the Kendall. When it was washed out
8 the resistance went up by a factor of three. When it was treated
9 with sulfuric acid it went back to the original value of about
10 32. And then the --

11 LACKNER: But --

12 HENNIGAN: The wicking rates were phenomenal. This
13 is a bonded material.

14 LACKNER: Has any work been done on wetting agents?

15 HENNIGAN: Mainly taking them out.

16 (Laughter.)

17 DANGELL: Hercules, which provided the fiber used
18 in the 1451 as a recommended wetting agent, I believe it's
19 QS3 by Rohm and Haas. They suggest that whatever surface active
20 agent they put on the fibers for textile handling ease be
21 removed and be replaced with this QS3. I don't know if any-
22 body -- Burroughs, who you dealt with, I presume, is the
23 leading proponent of this. I presume he would discuss this
24 with anybody who is interested.

25 HENNIGAN: Well, what is the amount of agent that

1 you could extract from Hercules material? I think it was on
2 the order of one-tenth of a percent.

3 DANGELL: Yes, one-tenth of a percent.

4 HENNIGAN: Right.

5 DANGELL: They recommend the removal with Stoddard
6 solvent, methyl alcohol. I don't know why sulfuric acid
7 was used. Maybe they have a good reason.

8 HENNIGAN: Well, the fellows at ESB thought these
9 oxidize the surface slightly, make it more wettable. Now it
10 didn't improve the wicking properties at all. In fact it
11 really didn't do it but just gave us better capacity.

12 FLEISCHER: I would like to know to clear my own
13 mind, how did you calculate to know how much electrolyte to
14 add to each of these cells and were they really very different
15 from one to the next?

16 HENNIGAN: I think they varied from 3-1/2 to 4 CCs
17 per ampere hours, is that about right?

18 VOICE: Approximately.

19 HENNIGAN: That is using the Pellon material, the
20 K4 took the most.

21 Bill Harsch?

22 HARSCH: Bill Harsch, Eagle Picher.

23 Tom, I'm just curious, when you are characterizing
24 these separators at ESB, were any of the separators tested to
25 the same type of test but under compression?

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1 HENNIGAN: You mean like absorption and so forth?

2 HARSCH: Yes.

3 HENNIGAN: They did try the Pellon material only,
4 the pellon materials only under compression and it was a
5 rather difficult test to run. I mean the plates will pull
6 the electrolyte out just like a blotter and there wasn't too
7 much uniformity. They tried samples of about three or four.
8 There wasn't too much uniformity there.

9 HARSCH: The reason I mention that is just in
10 handling the materials I myself haven't done any testing like
11 this but in handling the materials, the different polypropylenes
12 seem to have different compressive strengths. Some of them
13 are rather stiff and rigid and the others are very downy.
14 And I'm wondering whether the actual numbers we are looking
15 at don't change drastically under compression as they would
16 be when they in a cell?

17 HENNIGAN: Well, I don't know if we can look at
18 these properties -- as I said before, we are going to start
19 pulling these cells out to test, sending them to the materials
20 ranch here, and in the meantime we would like to come up with
21 -- we have the virgin materials that went into these cells.
22 And we would like to come up with a, try some more different
23 types of tests that might give us some correlation with
24 the data we have now and the cell test. Now maybe this
25 compression one would be a good one to go.

1 RAMPEL: I think that the loss in capacity may be
2 related to the progress of the discharge and the drying out
3 of the separator and, in other words, the particular separator
4 may have a tendency to hold less electrolyte to support the
5 full discharge, and you could check that by taking cell
6 resistance measurements, particularly as you cross over an
7 exhaust -- go on to three after hours and then fall down.
8 You may find that your separator is completely dried out.

9 HENNIGAN: That's one thing we can do. We do it
10 normally in the acceptance test. You mean do this during
11 the discharge, take out half the capacity and measure it?

12 Are there any further questions?

13 THIERFELDER: General Electric.

14 I was wondering about these capacities. What is
15 the definition of capacity, to a certain end voltage?

16 HENNIGAN: Yes, to one volt. The first data was to
17 one volt at C rate. And the last one was to one volt at the
18 C and C over 2 rate.

19 THIERFELDER: If the end volt can be picked at a
20 lower number, maybe the capacity of the polypropylene cells would
21 have actually come up. The given capacity to a higher end
22 volt.

23 HENNIGAN: Well, they were cut off at one volt.
24 When we do the acceptance test at Crane we can run them down
25 to zero.

1 THIERFELDER: I was wondering if the capacities
2 were compared down to zero you might get closer capacities.

3 HENNIGAN: We just got the cells going to acceptance
4 and test, so these are some things that we can do.

5 FALIK: As a person primarily interested in the
6 textile physics of it, I think you hit the nail on the head
7 as far as the function of wetting out properties go, whether
8 the substance is under compression or not. You may get
9 tremendous inneractions where something would be poor, not
10 compressed, and yet yet maintain this same degree of wicking
11 where a very compressible structure may have a lower wetting out
12 time. It should be looked at, I think, and I guess the
13 easiest way of doing it would be calendering these materials
14 to the same thickness they had when they were under compression
15 but of course then you get a contamination of the surface
16 glazing, and that may confound your analysis.

17 CARR: I have just a couple of things to say since
18 everybody else seems to be finished.

19 In these conferences sometimes it's a little hard
20 to recognize new information and I think really and truly
21 there is some new information, and I just want to point it
22 out that we took the wetting agents out of the cells or ESB
23 took the wetting agents out of the separators and we built
24 cells and if anything they ran slightly better, or in some
25 cases they ran better, which tends to make you believe that

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1 you might not need the wetting agent in the cell.

2 Now I am not saying that we do or we don't but
3 it was interesting. We were advised to let the cells stand
4 after activation for maybe a week before we would start
5 doing any tests on the cells, but we were kind of an impatient
6 lot anyway and we started the first charge on the cells in
7 approximately 48 hours after activation. Of course we were
8 watching very carefully to make sure that the voltages stayed
9 down and that the cells acted normally, and they did.

10 There was no change in charging characteristics
11 as we could detect from the first charge to the fifth or
12 sixth charge, indicating that there was any change of the
13 wetting characteristics of the separator which caused the
14 change in performance.

15 So I really think this is new information, and I
16 just wanted to point it out.

17 HENNIGAN: If there's no further questions here
18 we would like to move on to the area of seals.

19 As you know, years ago of course we had our
20 problems there. I won't tell you they are all solved. It seems
21 to be not too great, if the seal is built right, it's not too
22 great a problem any more. But that's a pretty tough statement.
23 But we have three people on seals. We would like to finish up
24 the seals session this morning and delay the -- going to lunch
25 until about 12:45.

jrbq70

1 And our first speaker is Bob Steinhauer from
2 Hughes Aircraft on a long life ceramic seal.

x 3 STEINHAUER: I would like to run through the salient
4 points that we should consider in metal ceramic seal design
5 for nickel cadmium space cells.

6 Metal ceramic structures have been used for
7 various applications. Earliest, I guess in the vacuum electron
8 tube industry, in nuclear fields for liquid metal cooling,
9 on Stanford linear accelerator which is another vacuum applica-
10 tion, in ion engines where you have plasma environments, space
11 nickel cadmium cells and more recently in gas lasers.

12 The seals must be designed for the application as
13 our cells may have to be. I would like to discuss the parameters
14 that must be considered in selecting a metal ceramic terminal
15 seal design for nickel cadmium cells for long life. By long
16 life I would define that as in excess of four, five years.

17 I would like to show the interactions of these
18 parameters and their affect upon the end product, and also
19 make the statement that I think metal ceramic terminal seals
20 have been used and that they are a good choice for this appli-
21 cation. And to recommend three different types of seals that
22 could be used for 10-year applications.

23 The content here has been refined on our low earth
24 orbit program for the Air Force at Wright-Patterson and we will
be testing three different types of seals.

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(Slide.) ①

The primary areas that must be considered are the ceramic body, the braze alloys used, the controlled or low expansion alloys and what metalizing or active metalizing or active alloys are used for bonding to the alumina-ceramic and then the geometry.

In the ceramic body, we should go to higher aluminas. We should go to small grain size to enhance both tensile and flexural strengths, minimum silicate content, because it's attacked by the KOH, and if you eliminate the silica you may want to consider, you could consider lower aluminas -- by low I mean certainly above 95 percent but with flex agents other than silica.

I would like to put a comparison table up here. These happen to be Coors bodies. The only reason I selected Coors at this point is that their brochure contains more data for comparison purposes than the competitors in certain cases, particularly with regard to crystal size.

(Slide.) ②

The crystal size is extremely important if you look as you go toward the higher aluminas it tends to drop off but as you go to smaller grain size it goes up. Now if we take this data and use a technique to get a straight line plot, namely a log log plot, for flexural strength, two points have been specifically ignored down here in this area because

(Slide) 3

1 they were some of the earlier developed bodies. These are
2 similar, whether its WESGO or American Lava body, the 85
3 and 90 percent bodies were developed specifically for
4 metalizing purposes. They metalize well but they are not good
5 for this application. The higher aluminas you will notice
6 do have a definite relationship to average crystal size to
7 flexural strength and this property is most important to us
8 for our application.

9 I want to point out the 99 percent body of low
10 average crystal size being fairly high value. What we are
11 typically using are bodies that range from 96 percent level
12 in here through the 995 level which in the case of Coors I
13 guess shows up as a lower strength body.

14 If you plot other manufacturers' data on top of this,
15 you will find similar relationships.

16 (Slide.) ④

17 The tensile strengths are similar.

18 (Slide.) ①

19 Now, trying to compare (Slide.) different ceramics
20 that may have been used in nickel cadmium seals and what the
21 flexing agents are, I would like to point out that this body
22 -- this is an analysis provided by American Lava at letter
23 request and this one also.

24 This high silica content is of some concern for
25 long term seals. I would prefer to see it down but maybe it's
not as harmful in the ceramic body as it may be in

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FOR NICKEL-CADMIUM SPACE CELLS
METAL-CERAMIC TERMINAL SEALS

KEY AREAS OF CONSIDERATION

- SEAL GEOMETRY
- ACTIVE METAL METALIZING, & ACTIVE ALLOYS FOR BONDING TO ALUMINA CERAMIC
- CONTROLLED EXPANSION ALLOYS
- BRAZE ALLOYS

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HIGH ALUMINA CERAMICS

[illegible]

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COORS ALUMINA CERAMICS

| BODY | MINIMUM # AL ₂ O ₃ | SYMBOL | AVERAGE CRYSTAL SIZE μ m | FLEXURAL STRENGTH Kpsi | TENSILE STRENGTH Kpsi |
|--------|---|--------|------------------------------------|------------------------------|-----------------------------|
| AD-28 | 0.20 | ○ | 7 | 43.0 | 25.2 |
| AD-40 | 0.40 | □ | 4 | 49.0 | 35.0 |
| AD-44 | 0.44 | ◇ | 15 | 21.0 | 28.0 |
| AD-46 | 0.46 | △ | 11 | 25.0 | 28.0 |
| AD-49 | 0.49 | ▵ | 25 | 48.0 | 31.0 |
| AD-50 | 0.50 | ▢ | 50 | 42.0 | 28.0 |
| AD-50S | 0.50 | □ | 19 | 48.0 | --- |
| AD-50S | 0.50 | ◇ | 3 | 42.0 | 42.0 |
| 1AT21V | 0.50 | ◇ | 50 | 41.0 | 30.0 |

23H00H

CERAMIC BODY

- OTHER FLUX AGENTS MAY BE ACCEPTABLE SUCH AS CaO
- MINIMUM SILICA CONTENT
- SMALL GRAIN SIZE TO ENHANCE TENSILE STRENGTH. I.E. 1-8 μm
- HIGH ALUMINA CERAMIC REQUIRED 99.9% Al_2O_3

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1 metalizing mix as I will comment on later. They do have
2 a 29.5 body as do other people. These generally are large
3 grain size bodies.

4 These two bodies that have been developed by
5 General Electric in their Schenectady labs have been used on a
6 seal that I would like to talk about later. The one point
7 that I would make is the large grain size, and the implications
8 from the previous chart.

9 One further point; specific notice to this Coors
10 AD99 body which showed up highest in flexural and tensile
11 strength. It is the highest flexural strength which is
12 highly desirable for what we are looking for. It has extremely
13 low silicate contents, in the 50 to 100 PPM range. It is
14 fluxed with magnesia Iutrea. This is a patented body by
15 Coors. Therefore, they freely provided this analytical data.
16 Those two fluxing agents and the low silica content and the
17 low crystal size are of extreme interest to us

18 (Slide.) (2)

19 In terms of braze alloys, the silver alloys should
20 be avoided because of possible migration problems even when
21 they are used in an alloy with another metal. Copper alloys
22 are compatible. We are using them with cell electric chemistry.
23 Nickel alloys may not be desirable because of a binary alloying
24 with titanium, but I am going to take exception to that state-
25 ment later.

1 The gold alloys are gold copper palladium or
2 perhaps gold copper nickel, are acceptable.

3 (Slide.) (2)

4 I asked our electrochemist, Jack Gillette, to
5 look into how copper, whether it would be acceptable or not,
6 and since it's between this point and this point, he states
7 that he can see no problem with using copper. I understand
8 that copper was used as a substrate in the Edison cell I
9 believe for the iron electrode.

10 VOICE: No.

11 STEINHAUER: No? Sorry.

12 These are several braze alloys that have been used
13 and could be considered. You will notice the liquidous points
14 go higher and higher in temperature. The higher the tempera-
15 ture you go, in general the thing that you are bonding to the
16 ceramic with the active element can degrade this ceramic
17 at shorter times of course at high temperatures and this
18 has to be considered.

19 The seal that I referred to previously at General
20 Electric, the business center and the people in Gainesville
21 have been working to develop a seal for nickel cadmium cells.
22 This is a patented process that makes use of the TINI3
23 eutechnic. This alloy is compatible with the alkaline
24 cadmium nickel cell environment.

25 I'm concerned with the silver in these alloys. We

1 have to be careful with this type of an alloy because of its
2 brittleness, which I will comment on a little bit later.

3 (Slide.) (9)

4 Using low expansion alloys to contact the ceramic,
5 you try to match the linear thermal coefficient of expansion
6 to the alumina that you are using. These are three possible
7 alloys that could be used. Alloy 42, the F-15ASTM alloy,
8 which is an iron nickel cobalt. And the alloy 52. You don't
9 necessarily have to use these alloys if you put these
10 ceramics in compression, but it's still better to use some-
11 thing that is near to the expansion coefficient and preferably
12 thin. By that I mean not to exceed 20 mills. Ten to 15
13 mills thickness is preferable.

14 Again there are numerous ceramic metal structures
15 made with thicker elements.

16 (Slide.) (1)

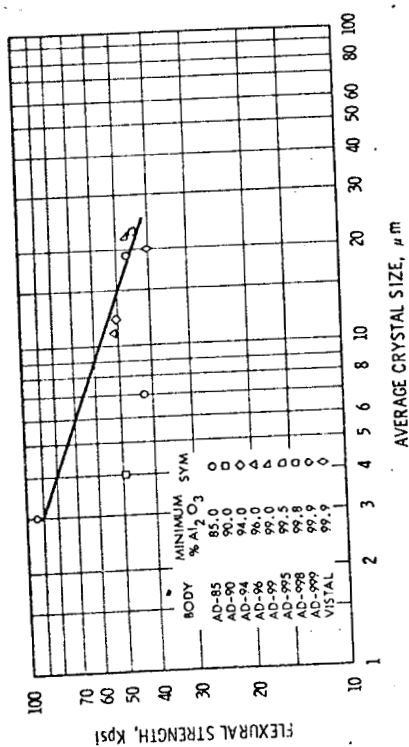
17 These are the chemistries and as you can see whether
18 you pick -- the only thing of significance is the difference
19 that this F15 alloy is slightly low in expansion coefficient.
20 The yield and tensile properties are roughly the same.

21 (Slide.) (2)

22 If we look at the expansion coefficient, the
23 materials of interest are the alumina, the alloy 52, 42,
24 F15 alloy, and then for comparative purposes, nickel, copper
25 and stainless steel.

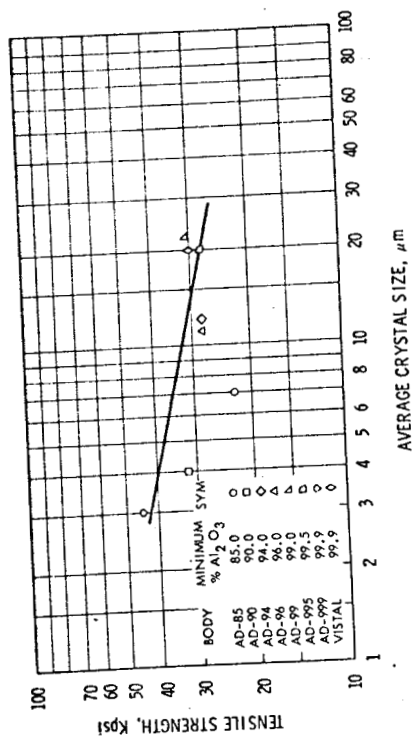
COORS HIGH ALUMINA CERAMICS

HUGHES
HUGHES AIRCRAFT COMPANY



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BRAZE ALLOYS

- SILVER ALLOYS SHOULD BE AVOIDED BECAUSE OF POSSIBLE MIGRATION PROBLEMS
- COPPER ALLOYS ARE COMPATIBLE WITH CELL ELECTROCHEMISTRY
- NICKEL ALLOYS NOT DESIRABLE BECAUSE OF BINARY ALLOYING WITH TITANIUM
- GOLD, 80 GOLD 20 COPPER, OR GOLD-PALLADIUM ARE CANDIDATE ALLOYS

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CERAMIC-METAL TERMINAL SEAL BRAZE ALLOYS

| BRAZE ALLOY | CHEMISTRY, WEIGHT % | LIQUIDUS, °C | SOLIDUS, °C |
|--------------------|---------------------|--------------|-------------|
| CUSIL | 72 Ag 28 Cu | 780 | 780 |
| PALCUSIL 5 | 68 Ag 27 Cu 5 Pd | 810 | 807 |
| GOLD-COPPER | 80 Au 20 Cu | 910 | 908 |
| GOLD | 100 Au | 1063 | 1063 |
| PALORO | 92 Au 8 Pd | 1240 | 1200 |
| Ti Ni ₃ | 21 Ti 79 Ni | 1380 | 1380 |

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jrbq76

1 It is possible to make metal ceramic seals between
2 thick piecew of copper and alumina. But again it narrows
3 your process tolerance down to the point where you have to be
4 very carefull and control your process much more carefully
5 than if you allow yourself a little more latitude.

6 (Slide.) (3)

7 There are different methods that can be used to
8 bond to the ceramic. I believe that the titanium and
9 sirconium systems are preferable. The titanium passivates
10 immediately and you cannot, in its oxide form, on the surface,
11 you cannot cause it to corrode.

12 In general there's three parts to a metal ceramic
13 bond. It's a crated seal similar to a quartz glass seal.
14 You are starting out with the ceramic, your active metal
15 ties in to either the ogygen of the ceramic or in the case of
16 a metalizing process you make that class E phase by
17 placing elements in the mix. Then you have metal -- a glassy
18 to metal transition and finally to your braze alloy..

19 This should have a two after it but this glassy
20 phase in the polymanganese as well as the molly itself, this
21 is soluble in KOH. The glassy phase in particular you can never
22 cover that glassy phase. It always sticks out from underneath
23 the ceramic where the COH can get to it and just go across the
24 seal. The molly is likewise soluble. As is tungsten. These
25 have been reported insoluble but the two people clean these

1 surfaces with alkaline solutions and long term tests have
2 shown that they are indeed soluble. I do not recommend molly
3 or tungsten.

4 Chromium is a nice system. It does not degrade the
5 ceramic but it is readily soluble in KOH.

6 The active alloys are -- have been used to braze
7 things like titanium to titanium. They can be used on
8 ceramic but they are a little bit difficult to handle. I
9 don't recommend their use at this point.

10 (Slide.) (4)

11 That may be a little hard to see but the types of
12 seals that we have been using are the stress relief type.
13 Mainly they have a low expansion alloy that can take up dif-
14 ferences in expansion between the stainless steel and the
15 ceramic.

16 One of the failure modes has been a misalignment.
17 I can show that. (Slide.) It doesn't matter whether you use
18 the geometry at the top here of this one. The ceramic can
19 misalign to the point where it hits the post at the stress
20 relief collar. This point here -- excuse me.

21 At the cuff and at the cup. The problem -- let me
22 think about that. No. It can hit the post at this point
23 and at this point causing the braze alloy at the cuff to go
24 to zero and there is not a corrosion type of leakage but a
25 tortuous path that eventually the KOH comes through.

ELECTROCHEMICAL COMPATIBILITY OF COPPER BRAZE ALLOYS



| | | |
|--------------------------------|--------|-------|
| $H_2O \rightarrow H_2$ | -0.828 | 0.000 |
| $Cd(OH)_2 \rightarrow Cd$ | -0.805 | 0.023 |
| $Cu_2O \rightarrow Cu$ | -0.361 | 0.467 |
| $CuO \rightarrow Cu$ | -0.258 | 0.570 |
| $Cu(OH)_2 \rightarrow Cu$ | -0.224 | 0.604 |
| $O_2 \rightarrow OH^-$ | 0.401 | 1.229 |
| $NiOOH \rightarrow Ni(OH)_2^*$ | 0.49 | 1.32 |

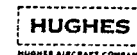
* $NiO_2 \rightarrow Ni(OH)_2$

METAL-CERAMIC TERMINAL SEALS LOW EXPANSION ALLOYS



| CHEMISTRY | ALLOY 42 | ALLOY 52 | F-15 ALLOY |
|--|-----------------------|-----------------------|-----------------------|
| Ni | 42.0 | 50.5 | 29.0 |
| Fe | BAL. | BAL. | BAL. |
| Co | -- | -- | 17.0 |
| Mn | 0.50 | 0.50 | 0.30 |
| Si | 0.25 | 0.25 | 0.20 |
| C | 0.05 | 0.01 MAX | 0.02 |
| Ti | 0.40 | -- | -- |
| PHYSICAL | | | |
| THERMAL EXP., $^{\circ}C^{-1}$, 25-800 $^{\circ}C$ | 12.1×10^{-6} | 12.5×10^{-6} | 10.3×10^{-6} |
| TENSILE STRENGTH, Kpsi | 80.0 | 80.0 | 75.0 |
| YIELD STRENGTH, Kpsi | 34.0 | 40.0 | 50.0 |

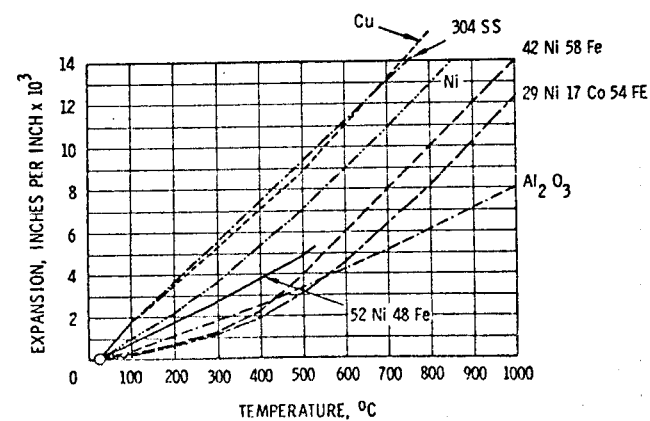
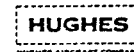
CONTROLLED EXPANSION ALLOYS



- METAL HARDWARE CONTACTING CERAMIC BODY SHOULD EXHIBIT
LOW LINEAR THERMAL EXPANSION

| | | | |
|------------|------------|----------|------------|
| ALLOY 42 | 42% NICKEL | 58% IRON | |
| F-15 ALLOY | 29% NICKEL | 54% IRON | 17% COBALT |
| ALLOY 52 | 52% NICKEL | 48% IRON | |

EXPANSION CURVES FOR MATERIALS USED IN METAL-CERAMIC TERMINAL SEALS



jrb-78

1 We have observed in both types of seals, this,
2 and it's usually less than a half a percent of the sample that
3 we have. A simple alignment would get around that problem.

4 These seals of this geometry may well be able to
5 be made into the long life seals. The problem is that it
6 requires a ductile alloy. It's very sensitive if you attempt
7 to put a brittle alloy in there and you have to watch out
8 for things that will react with titanium.

9 Again, the higher aluminas, thin elements,
10 matching coefficients of expansion in this case the ductile
11 alloy. The seal shown here is the one developed by General
12 Electric. The system of using nickel titanium, these are
13 high expansion but it is used in a controlled manner. The
14 materials are compatible. Perhaps this should be a weld
15 rather than a braze or a different braze alloy.

16 It does use the ceramic back up rings. This is
17 a butt seal geometry or what I call electron gun structure
18 as contrasted to a stress relief geometry.

19 These back up rings at first seem superfluous.
20 They are indeed important.

21 This is another type of seal that has been used on
22 recent programs. I would like to confine my remarks to the
23 stress relief and the butt seal type of geometry today.

24 We are looking at another version (Slide) of butt
25 seal geometry on our program. It will have a stress relief

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1 member in it and the ceramic backup rings. These backup
2 rings add one and a half to two times the tensile strength
3 to the ceramic structure simply by adding rigidity to this
4 member or this member.

5 (Slide.) The only reason this is turned down is
6 to lower the height which we find convenient in cells
7 that we fly at Hughes. This will be made with an active
8 metal mix type of process. We will be using the 999 alumina
9 from Coors in this structure. We will be evaluating this
10 seal which may not be exactly the final design. (Slide.)

11 This one and this one, with perhaps different
12 braze alloys in here. There is no -- this is not to degrade
13 this seal. I feel that these are of equal quality when the
14 process is controlled.

15 With regard to the ceramic used on the GE seal,
16 my only comment would be that if the small grain size material
17 were used, it could greatly enhance the tensile strength
18 of the structure, particularly in light of the expansion
19 coefficient of the nickel used.

20 May we have the lights, please.

21 In summary, I would like to say that the active
22 metal or systems using titanium are preferable for our
23 application. However they are one shot processes, which is
24 not objectionable here. Namely, the whole metal ceramic is
25 made in one pass through a vacuum furnace in contrast to a

1 moly manganese process which can be used essentially and why
2 it's preferred in the tube industry. They can build up very
3 complex structures by using braze alloys that are 10 to 15
4 degrees C lower so that they can build up the whole sequence
5 of 10 different brazes.

6 The moly manganese with its glassy phase is not
7 desirable. There is something else to note. Namely that in
8 the stress relief type of seal you are making your bonds
9 to the circumferential surfaces. This generally means you
10 have to paint the mix on by hand. It's a handbrush operation
11 and a machine revolves the ceramic, whereas in the butt seal
12 structure, because of the flat surfaces, you can, it can
13 lend itself to a silk screening process that can perhaps
14 be controlled to a better extent as far as thickness.

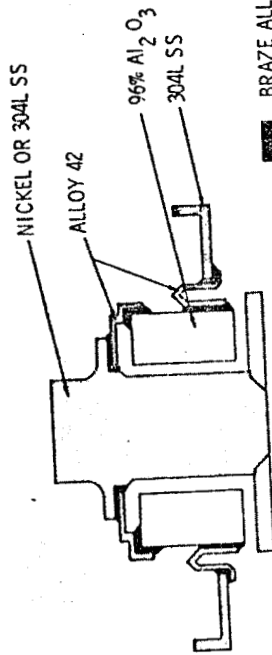
15 Further, the butt seals can make use of braze forms
16 of generally two mills thickness that will control the braze
17 alloy thickness and also the butt seal is not sensitive to this
18 alignment problem that I referred to before on these two
19 seals.

20 The other problem is that in a stress relief type
21 seal you are generally requiring your braze alloy to float
22 down or to flow up whereas the braze alloy in a structure
23 (Slide) like this being a braze form of say 2 mills thick is
24 right there. All it has to do is melt or flow.

25 I tried to put into perspective the different

HUGHES
HUGHES AIRCRAFT COMPANY

STRESS RELIEF GEOMETRY TERMINAL SEAL



BRAZE ALLOY
80 Au 20 Cu, Au or
92 Au 8 Pd

HUGHES
HUGHES AIRCRAFT COMPANY

ACTIVE ALLOYS

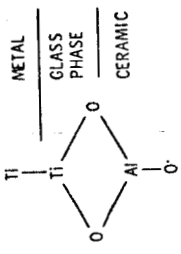
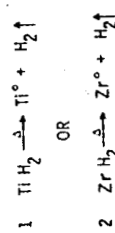
- Ti Cu Ag
- Ti Cu Ni
- Al Ti Zr Be

METALIZING PROCESSES

- Mo
- Mn O₂
- Ti O₂
- Fe₂ O₃
- Si O₂
- Mo
- La₂ O₃
- W
- Cs
- Cr
- Au
- Cu

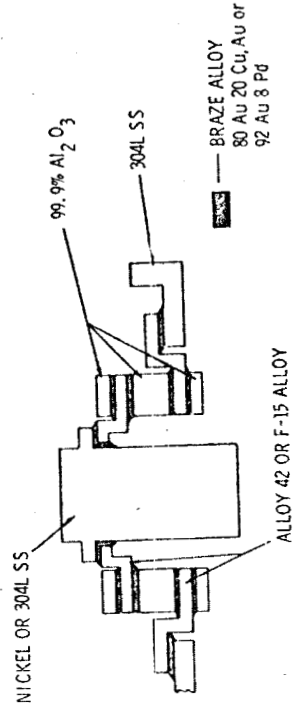
CERAMIC BONDING

- ACTIVE METAL PROCESSES



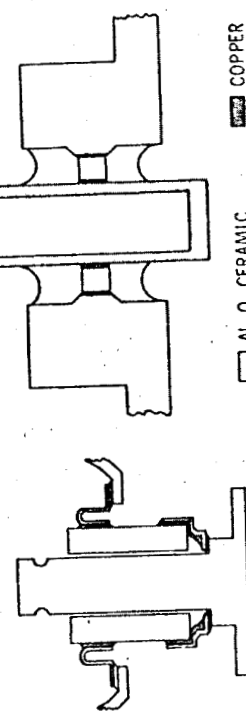
HUGHES
HUGHES AIRCRAFT COMPANY

ELECTRON GUN GEOMETRY TERMINAL SEAL (BUTT SEAL GEOMETRY)

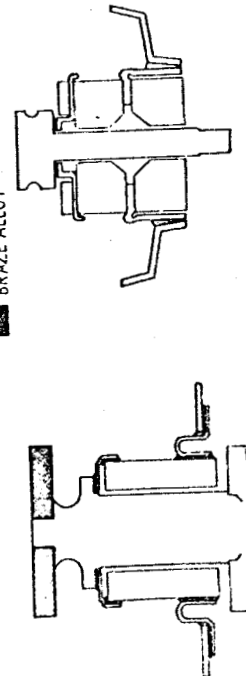


BRAZE ALLOY
80 Au 20 Cu, Au or
92 Au 8 Pd

HUGHES
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- Al₂O₃ CERAMIC
- COPPER
- GLASS
- NICKEL OR 304L SS
- 304L SS
- LOW EXPANSION ALLOY
- BRAZE ALLOY



1 things that we must consider and how they interact. I am
2 sure I have only just touched on the surface.

3 Thank you.

4 (Applause.)

5 HENNIGAN: Do you have any questions for Bob
6 Steinhauer.

7 Dr. Will?

8 WILL: Will, G.E. I would like to comment on the
9 use of copper alloy brazes in batteries. While you are
10 completely correct in that when copper is used in a negative
11 plate this use is all right and this is because there is
12 cathodic protection involved for the copper used in the
13 negative plate.

14 However, one can consider the brazed material as a
15 piece of electrode, an open circuit, and you can therefore
16 no longer apply the thermodynamic data which you have presented
17 in one of your tables. Under those conditions, when you have
18 the presence of oxygen, which is something during overcharging
19 of the cell, and in the simultaneous presence of KOH, copper
20 acts as an exceedingly efficient getter for oxygen recombination.
21 You form first cuprous oxide, which is highly insoluble.
22 However then it is unavoidable that you form cupric hydroxide
23 which dissolves exceedingly efficiently as cuprate ions.

24 STEINHAUER: The seals that are used do use the
25 copper but they do have protection, I should add. The

1 The suppliers either use materials that cover the copper surface
2 -- this is one way of getting around that.

3 COHN: Cohn, NASA.

4 Do you have any data on fatigue life as a function
5 of pressure cycling both the number of cycles and the extent
6 of excursion in pressure.

7 STEINHAUER: No, but I think for the pressures that
8 we are talking about, this would not be too much of a factor.
9 The active metal seals generally have tensile strengths in
10 range of six to eight thousand PSI and the molybdenum seals
11 are well up in the 15,000 range.

12 COHN: It may surprise you to learn that for the
13 implant batteries for the heart pacers, the mode of failure is
14 not that the battery gives but that the wires break so
15 you may find that you will get some surprises when you make
16 some actual tests about what happens when the seal is
17 pressure cycled.

18 STEINHAUER: Could I comment to that. On qual
19 level vibrations, which is where I would be particularly
20 concerned, we have never seen a failure at a seal, spacecraft
21 shaking or a battery shake test.

22 BOWER: Do you have a method of accelerated testing
23 on these seals? We are talking five to ten years.

24 STEINHAUER: No, our plan is really to immerse them
25 in KOH solutions, apply potentials just below the gassing

1 potentials and cycle them with positive and reverse polarities
2 metallurgically cross-sectioned and, and also analyze the
3 solutions. We may run microameter corrosion checks on
4 the materials that are used. Unfortunately this is a small
5 portion of our program percentagewise and we can't go into
6 it in the depth we would like to.

7 HENNIGAN: John Leuthard?

8 LEUTHARD. Leuthard. Martin Marietta.

9 Am I right, I want to understand something. In
10 this ceramic, when we are talking about 99.9 percent minimum
11 alumina, is the other one-tenth of a percent the controlled
12 number of elements and have a reason for being in this
13 total mixture, or what is the 99.9, what does it mean?

14 STEINHAUER: It means you are guaranteed that
15 minimum. You generally have to have other fluxing elements
16 in the body when it is fired at high temperature to cause
17 those particals to adhere. You are bringing up a very
18 important point. We must know what the other tenth of a
19 percent is. And that is why I was dwelling on that one table
20 which fluxing agents are preferable.

21 LEUTHARD: That's what made me think of it.
22 When I saw different elements in different columns, there must
23 be a reason for those elements--

24 STEINHAUER: Yes. In general, my recommendation is
25 to minimize silica but you could put in things that are not

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1 bothered by the KOH. In other words, you may well be able
2 to use a lower than a 999 body if the other minor percentage
3 elements are compatible with our system.

4 LEUTHARD: Then is the selection of the purity and
5 the additional elements that are within this total compound
6 a function of the manufacturer for that particular ceramic?

7 STEINHAUER: Yes. The ceramic must be carefully
8 selected. The third think of course is the crystal sizes.
9 That is the flexural strength.

10 HENNIGAN: Steve Gaston.

11 GASTON: I didn't notice in your sketches any
12 parting materials in the void areas which are quite often used.
13 In your program do you plan to use any parting materials to
14 fillethese void areas?

15 STEINHAUER: I believe that the materials useage
16 should have integrity in itself and therefore we would
17 prefer to leave those parting or auxiliary aids to preclude
18 attack of seal out and to evaluate the materials that we have
19 in the seal. If we put in the parting materials it may cloud
20 the results.

21 GASTON: I have one more comment, on the 99.9
22 percent Coors material, there is a substantial cost increase
23 going into that material, I heard?

24 STEINHAUER: Yes. In R&D quantities which I just
25 checked into that cost increase can be something like 16 times.

1 However, in quantities that we would buy for a spacecraft
2 program, that may only be a factor of, I don't know, two to
3 four. Projecting that into the cost increase on the metal
4 ceramic structure that may only mean an increase of somewhere --
5 see the ceramic is not the total cost. The structure may
6 increase by \$5 to \$10, apiece.

7 HENNIGAN: Wil Scott?

8 SCOTT: Scott from TRW.

9 Sometime ago in discussing this problem with I
10 believe it was American Lava, they made the point that they
11 felt that it was not, I won't say possible, but not practical
12 to make a braze to alumina bond without having a reasonable
13 level of silica content in the ceramic material because they
14 could not get adequate strength to the bond. And they were
15 talking about levels of silica well in excess of a few tenths
16 of a percent. Would you comment on that?

17 STEINHAUER: Yes. Different metalizing processes that
18 are used around the country, if you want to go after
19 proprietary things, those are the most proprietary that I have
20 seen in the tube field. You either have to have a glassy
21 phase that I mentioned in the ceramic or in the metalizing
22 that you apply to it. Now the nice part about the glassy phase
23 and the active metal mix or the GE process is that it uses
24 the oxide of the ceramic itself. Namely the alumina. Also,
25 American Lava is in the ceramic metalizing structures field

1 too and what you find is possible at one supplier is not
2 necessarily true at another. It just depends on the process.

3 I am saying that it can be done with this high
4 level of alumina and as an example of that I point to the
5 vistal or lukolux which is an extremely high alumina and
6 can be done with these processed.

7 SCOTT: You showed I believe an increase in a
8 factor of two in the flexural strength of the ceramic material
9 in going from 95 or so to 99 plus percent.

10 Do you consider that factor of two in that range
11 of strength very desirable or necessary?

12 STEINHAUER: Yes, from the standpoint of the
13 point that I was making about the brittleness of the braze
14 alloy. Where you have to worry is right in that place where
15 you are forming the glassy phase, and particularly in the use of
16 titania. It will penetrate into the ceramic causing a failure
17 -- namely, a weakening of the ceramic itself. And therefore,
18 I consider this a very significant point.

19 If you will notice the three nines alumina, the
20 small grain size versus the vistal or TE has alucolux of
21 large grain size you can see the difference -- same purity
22 material but different grain size.

23 SCOTT: I gather that this difference is most
24 important if you go to some of the harder and less ductil
25 brazing alloys. Is it as important if you use the more
ductil silver copper alloys.

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1 STEINHAUER: No, it is not, that's correct.

2 SCOTT: One last question. You I think rightly
3 so generally mentioned the problem of silver. But have you
4 actually observed cases of silver migration causing a
5 problem in any of the recent vintage of terminals produced
6 in the last few years in nickel cadmium cells?

7 STEINHAUER: Personal observations, no. And
8 perhaps the organics, the filling materials are precluding
d Tape 2 9 that problem.

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1 The eutectic alloys would definitely inhibit this but it won't
2 stop it.

3 HENNIGAN: A comment from the fellow from Ceramaseal?

4 BREDBENNER: (Ceramaseal, Inc.) I just want to make
5 two comments on the nickel titanium butt seal approach that
6 Bob was discussing.

7 At the temperatures that this seal must be made,
8 titanium becomes a tremendous getter and it will absorb
9 everything in sight, including primarily oxygen, one of the
10 materials, which requires real close processing and tremendous
11 vacuum, probably in the range of 10 to the minus 8 tor or
12 better, which is a real problem in achieving in most cases.
13 It requires real special equipment.

14 Secondly, this material that it does getter, when
15 the braze melts the nickel-titanium eutectic is formed and any
16 of these materials that have been gettered produce a slag which
17 floats to the junction of the seal; and on solidifying you have
18 a pretty junky seal.

19 HENNIGAN: We would like to move on to the next
20 speaker. If there are further questions -- well, one more from
21 Mr. Turner.

22 TURNER: (Ceramaseal, Inc.) Bob, when you talk
23 about the high silica bodies and failure because of the silica
24 in the body, so you expect that if you use the high silica body
25 such as the lava body with 3 percent of silica or more, would

1 you expect the failure through the body or through the seal
2 adjacent to the area where the seal is connected to the body?

3 STEINHAEUER: Probably adjacent to the area but,
4 again, I am pointing out desirable things. I have never seen
5 a failure of this type. The high silicon in the body may be
6 perfectly acceptable for ten years, but we are talking about
7 the difference between the terminal seals that we have used
8 and tested, for instance on the NED? crane programs two,
9 four, five and six years versus missions we have to look into
10 now in the seven to ten year category.

11 In other words, we just don't know whether these
12 seals will go that long and we ought to be thinking about
13 upgrading them.

14 HENNIGAN: We would to move on to the next speaker
15 here, Mr. Ed McHenry of Bell Telephone, who is going to talk
16 on the Modifications to the Ziegler Seal.

17 MC HENRY: (Bell Telephone Lab) This will just be
18 a review of the talk I gave at Atlantic City.

19 The first thing I would like to talk about is the
20 thermal cycle test that we use to evaluate our seals. It is
21 sort of a qualitative test and we felt that with a plastic
22 compression seal, we don't have too much in the way of
23 chemical problems except perhaps nylon will eventually at
24 higher temperatures dissolve. But generally I think the
25 plastic seals fail due to fatigue. The oxygen pressure changes

1 inside the cell and the change in temperature will cause a
2 thermal compression and contraction of the gasket material,
3 so we chose this thermal cycle test to essentially give us
4 a fatigue test which probably is the major cause of failure.

5 (Slide.) (2)

6 Here I show the thermal cycle test that we used.
7 We used temperature extremes of minus 40 and plus 160 F.
8 because these are the extremes that we expect not to exceed
9 in Bell System use.

10 It was a two-hour cycle; it is about 40 minutes at
11 the low temperature; it took 20 minutes to go up to the higher
12 temperature and then 40 more minutes at the high temperature
13 and 20 minutes down to the lower temperature.

14 This cycle was continued 24 hours a day, seven
15 days a week, so we get 12 cycles a day. We would test them at
16 the end of each day for the first week so would have every 12
17 cycles. The test method was simply to wet some wide-range
18 pH paper and place it on the seal and leave it there for about
19 five minutes and any KOH that had leaked out would be indicated
20 by a change in pH, and a pH of about nine was considered to
21 show that we had leaked enough KOH to call the cell a leaker.

22 (Slide.) (2)

23 Here we show seal performance at constant overcharge
24 versus thermal cycle. The A, B, C and D were D cells of
25 various manufacturers; they were tested at constant overcharge

1 at various temperatures, different cells in the same group.
2 Some were run at 32, some at 20 F. and some at room temperature.
3 This is just a conglomerate of all of them.

4 There was one particular manufacturer where none
5 of their seals failed and some were better than others.

6 We ran cells of the same group, not the same cells
7 that we had run at the top there, but cells taken from the
8 same lot were run on thermal cycle and we find that the A is
9 much better on thermal cycle than B, C, and D in the same
10 order.

11 This is a qualitative test, you don't exactly
12 predict the number of days anything is going to last but you
13 can say that A is better than B and that B is better than C.
14 And we see that it took 20 days to do the same thing we
15 learned in 240 days.

16 So it seems to be a pretty good qualitative test
17 to tell whether you have a good seal or bad seal. Generally
18 speaking, in our observations of all the seals we have used,
19 this does follow -- the A is always good no matter what we do
20 with it and they do stay in that same qualitative order.

21 (Slide.) ③

22 Here we show the Ziegler seal developed for
23 submarine cable a long time ago. It consists of a nickel
24 barrel that is brazed into the lid of the cell. We have a
25 kelly bushing which screws into the nickel barrel and the

1 lead wire is inserted inside the bushing. This thing is
2 compressed; it is reduced in diameter by about 6 percent from
3 250 thousandths down to 234. This compresses the bushing and
4 the threads prevent the bushing from extruding out the ends
5 and maintains a very high hydrostatic pressure in the middle.

6 These things will take something like 30,000 pounds
7 per square inch hydrostatic pressure for submarine cable work,
8 so they withstand more pressure than the cam will.

9 We had used them on some experimental Telstar
10 batteries. We had about 50 of these and 50 glass seals and
11 400 ceramic-to-metal seals, but these we made eight years ago
12 and were of the moly manganese type -- the ceramic seal was,
13 the binder there. I don't know much about it but that is what
14 it said it was.

15 Perhaps the newer ceramic-to-metal seals have
16 avoided some of the problems that these old ones had. But we
17 found that all the glass seals leaked within about four years.
18 This was at constant overcharge, about C over 100, I believe
19 it was, and room temperature. All the cells had run through
20 a preliminary vibration test, simulating rockets and a couple
21 of characterization cycles, but, generally, essentially all we
22 had was about four years of constant overcharge at C over 100
23 and then another four years of just open circuit stand.

24 At the end of the four years we found that all of
25 the glass-to-metal seals were leaking, half the ceramic-to-

1 metal seals were leaking. At the end of eight years we have
2 everything but the Ziegler seal leaking and none of these had
3 leaked at all, or at least to where you could detect with the
4 pH paper. A calculation of the gas permeabilities and all
5 says you lose about 1cc atmosphere per 1,000 years of oxygen
6 diffusing through this, provided it doesn't have a leak path;
7 but if it just has to diffuse through the plastic there really
8 isn't much of a problem there.

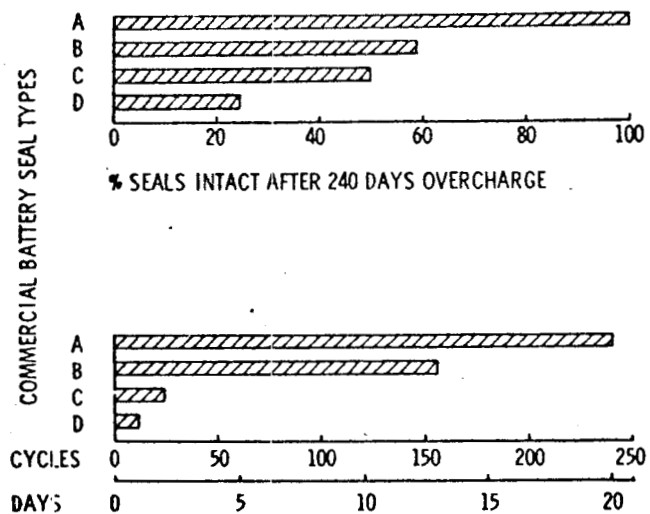
9 The problem with this seal is that you do have to
10 machine the threads very carefully; they must match exactly
11 and you have to use this rounded Whitworth thread so that
12 when you compress you don't have sharp roots in the bottom of
13 the threads because they will leave a helical leakage path
14 and the seal would fail.

15 So it does have to be carefully machined with the
16 special thread, but if done correctly it works very well.

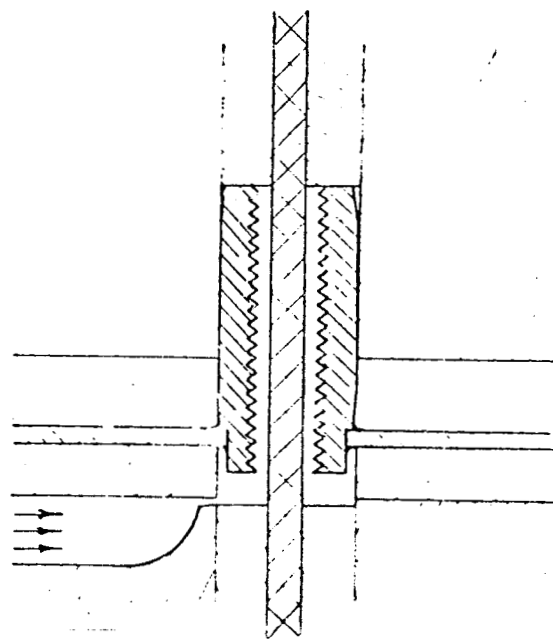
17 (Slide.) ④

18 Here we have gone to injection molding to form
19 our bushing. The yellow portion is the injection molded
20 material; the red is the nickel barrel which is brazed into
21 the red lid; and the green is the lead wire. This can be done
22 very simply and easily and it avoids the use of a carefully-
23 machined thread. You can cut the thread with anything. We
24 used an old, dull, 8/32 tap to just cut some sort of thread in
25 there and then your injection mold.

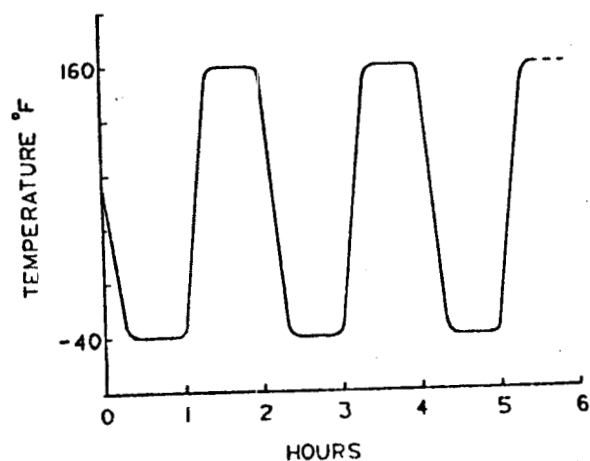
SEAL PERFORMANCE CONSTANT OVERCHARGE VS THERMAL CYCLE



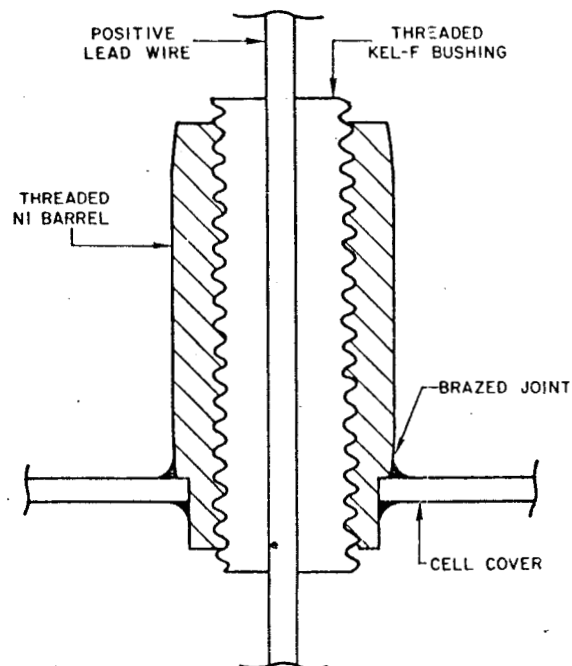
INJECTION MOLD FOR ZIEGLER SEAL



THERMAL CYCLE TEST TEMPERATURE PROFILE



CONSTRUCTION OF ZIEGLER SEAL



1 I did use nylon 6/6 for this. I used a number of
2 nylons. The nylon 6/6 was best in the sense that it takes
3 more heat when you weld the cover on; you tend to heat the
4 thing up, but ideally you weld the cover on before you crimp
5 it then you don't have to worry about any kind of problems
6 there.

7 (Slide.) (F)

8 This shows the difference in threads. The top thread
9 was machined by one of the local machine shops. It is very
10 uniform and both of these seals have been cycled and the bottom
11 thread shows injection-molded seal, and you cannot really do
12 much worse a job of threading it; but this is perfectly adequate.

13 You have no trouble with this kind of thread. We
14 had no leakage of any kind.

15 (Slide.) (U)

16 Here I show the BTL which consists of all the
17 Ziegler seals; these are injection-molded or the kel-F machine.
18 The other lines are the A, B, C and D of the previous bar graph
19 but they were of a later manufacture date. It is a D cell of
20 the same manufacturer but apparently, well, at least the one
21 seal went 1600 or 2,000 cycles without failure. A couple
22 of them did, but in general these are just regular D cells and
23 they fail very early in this kind of test.

24 You can see the Ziegler seal is much, much better.
25 In fact, at 2,000 cycles it shows no failure whatever, so I

1 feel that you just aren't going to get that much fatigue in
2 normal lifetime. If they do fail it will probably be from
3 long-term chemical attack on the nylon.

4 We didn't do any kel-F seals because we couldn't
5 injection mold them. Apparently you can injection mold the
6 kel-F but we can't, not on the machine we have in the lab.
7 This represents nylon injection molding and the Ziegler seals.

8 Then we tried to use the same principles as used
9 in the Ziegler seals but we tried to make it a little bit
10 cheaper.

11 (Slide.) 

12 On this slide we developed a new type of seal.
13 Here we just have a metal tubing. You can make it as long as
14 the cell. You put a plastic tubing inside that and the lead
15 wire and crimp it every eighth of an inch. It doesn't have to
16 be an eighth of an inch but I did it every eighth of an inch.

17 Then this thing is welded on top of the cell. I
18 didn't show a safety vent or anything of that kind. You would
19 have to put something of that kind in the fill tube,

20 This is a very simple seal to put together; it can
21 be made in any length. It has the advantage that if you
22 change the design of the cell a little bit you don't have to
23 change the design of the seal; you just braze it into a little
24 bit bigger top or smaller top. Or you can cut it a little bit
25 shorter, but there is no great change in design required.

1 The crimping is exactly the same.

2 Now I have made cells of various kinds using this
3 seal. I have some that are 3/8" long with only two crimps.
4 I would have a graph of the data except that it is exactly
5 the same as the Ziegler seal data. They don't leak if you
6 use a nylon tubing there. I used nylon 6/6.

7 They just cycle on and on for a thousand cycles
8 to two thousand cycles. I just don't have any failures.
9 There is one way you can make them fail, you can overheat
10 them. If you run them up over 200 F. the plastic will begin
11 to relax and it won't hold its compression; but the thing is,
12 you have to avoid heating them that high.

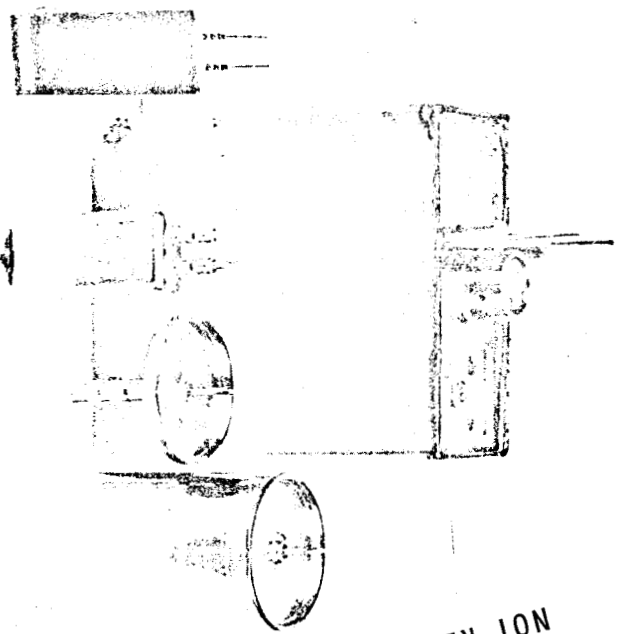
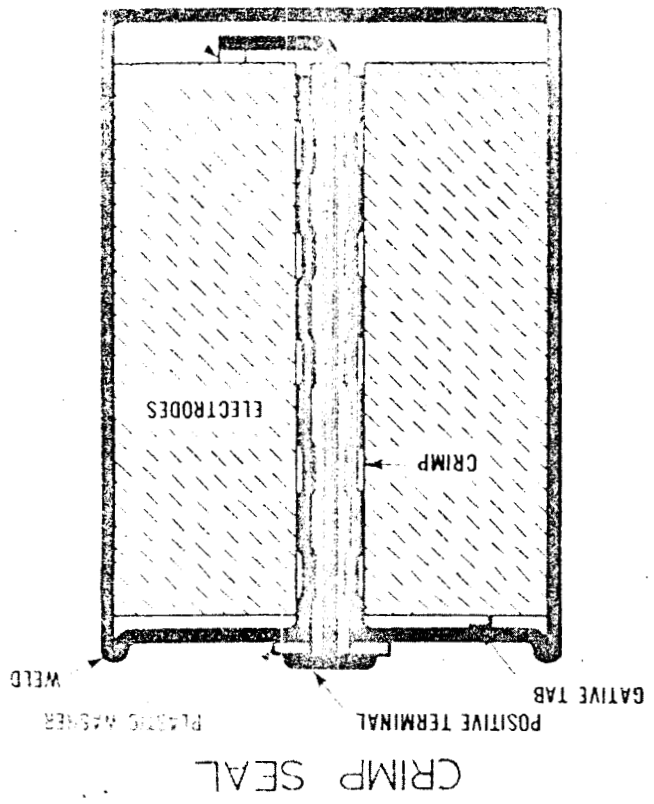
13 You can also injection mold this kind of seal,
14 So when you injection mold you essentially avoid all the
15 assembly problems; you cannot scratch the plastic tubing or
16 anything of that kind. It is very easy to put together. You
17 don't need much in the way of high caliber people. It is very
18 quick. It should be quite cheap.

19 I suspect you could make them for probably 15 or
20 20 cents. You just need a tube and you braze a hole bunch of
21 them in one shot. You just put it in a crimper and crimp.
22 So it is not an expensive sort of thing.

23 (Slide.) ⑨

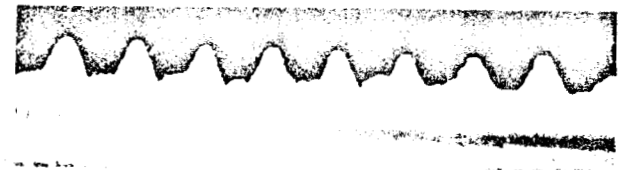
24 Here we show some of the little cells that I have
25 made. This D cell here has this type of seal in it; it extends

PLASTIC TUBING

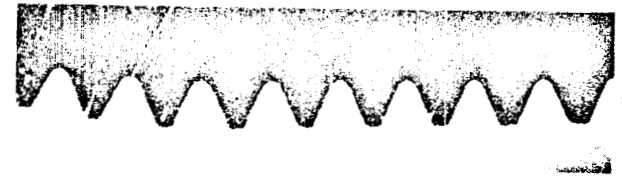


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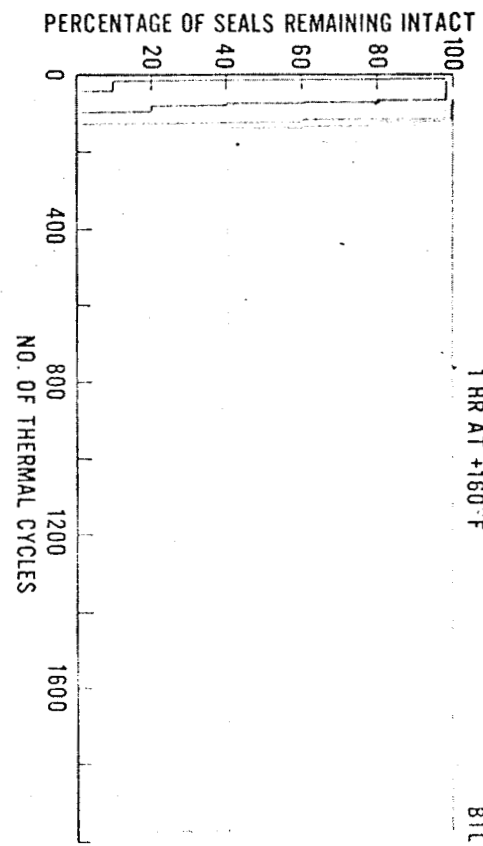
INJECTION MOLDED



STANDARD



THREAD DESIGN FOR ZIEGLER SEALS



THERMAL CYCLE LEAK TEST

1 HR AT -40°F
1 HR AT +160°F

8TL

1 down inside the cell. That was injection molded and it is a
2 little bit rounder than the others, but you can make them of
3 various sizes.

4 The bigger cell is this 20 ampere-hour cell with
5 two Ziegler seals injection molded on the top of it.

6 Then we have two 3/8" long seals, they are 1/8"
7 in diameter and 3/8" long. On the end there is a little small
8 cell we have which is a 100 milliamper-hour cell with two
9 50 mill diameter seals, the outside diameter of the seal, and
10 they are 3/16" long, I believe, and they have a 15 mill wire
11 running through them.

12 That is a polypropalene tubing. All the rest were
13 nylon but that particular one we used polypropalene because
14 what we did was coat the wire. If you get very, very small,
15 the tolerances that you require, the 1 mil tolerance that you
16 use to put your tubes together is a good portion of the total
17 diameter so that you don't want any slop if you can avoid it.
18 If you coat the wire you don't have any tolerance between the
19 wire and the plastic tubing on the inside.

20 These have all gone over 1,000 cycles, thermal
21 cycles, except for the polypropalene which has gone 200 and
22 some cycles and I don't know whether it is going to fail or
23 what it is going to do.

24 That is essentially all I have.

25 (Applause.)

1 HENNIGAN: Do you have any questions for Mr.
2 McHenry? We have time for a few.

3 Bill Harsch?

4 HARSCH: (Eagle PitcherCo.) I am just curious
5 about the seals that you had on test, I think you said, eight
6 years?

7 MC HENRY: Yes, these were the Ziegler seal, the
8 machined kel-F bushing and they were carefully assembled.

9 HARSCH: Have any of these seals been taken off
10 of test and say, cross-sectioned under anything like that?

11 MC HENRY: No, we haven't taken any off. I have
12 one that I should have done that to. Deal will say why
13 haven't I, but I haven't actually done it yet.

14 HARSCH: I am just wondering if there is a
15 potential leakage path where it is in the seal?

16 MC HENRY: I didn't do any of the work on this,
17 of course; that was done years ago. There were some higher
18 temperature tests done originally where they put them in KOH
19 and stewed them in oxygen and things and raised the temperature;
20 when they got up over 200 -- I think it was 250 or so F. --
21 you did get leakage paths up along the thread; but as you get
22 too hot the kel-F simply cannot support that pressure anymore
23 and it begins to extrude.

24 But is is just not a high-temperature seal;
25 generally speaking, say if you use a nylon separator you

1 cannot heat it anyway.

2 HENNIGAN: Mr. Bredbenner from Ceramaseal?

3 BREDBENNER: My question is, what diameter can you
4 go to in this? I would imagine this type of seal is limited
5 in maintaining hydrostatic stress on that kel-F as the
6 diameter increases?

7 MC HENRY: I am not sure; we haven't gone up. I
8 think there was a government contract where somebody did.
9 They scaled up -- I think it was Texas Instrument -- scaled
10 up some of the Ziegler seals and they were perfectly fine
11 except you couldn't sterilize them. But otherwise they
12 stood up very well. I think with about 1/8" diameter wire
13 or something of that kind.

14 VOICE: 1/4" diameter.

15 MC HENRY: 1/4" diameter? So I think you can
16 scale them up, but I would imagine though what you would do
17 is -- the thickness of the wall of the plastic would probably
18 remain about the same. In other words, right now you have
19 a 50 mill wire and about a 50 mill wall of plastic. I
20 think even if you had 1/4" cam in the wire you wouldn't
21 want to make that plastic much thicker.

22 I don't really know. I don't see any reason why
23 it wouldn't and it doesn't seem to in what scaling has been
24 done. But I couldn't answer that.

25 The one think you would have to avoid is, if you

1 short your battery and get a very heavy current to this wire
2 you have to have a hefty enough wire that it won't heat to
3 the point where you melt your seal, but in a spacecraft if you
4 short out the battery I presume there is nothing you can do
5 about it anyway.

6 HENNIGAN: There is time for one more question.

7 We would like to move on because Dr. Park might
8 have something planned this afternoon and we will try to get him
9 in before lunch.

10 Bob Steinhauer? Will you be here this afternoon?

11 STEINHAUER: (Hughes) Not on the seals, but out of
12 curiosity, on the B cell, how did you make that negative tab
13 weld; it doesn't seem like you have too much room there?

14 MC HENRY: How did we make the negative tab weld?
15 Let me see.

16 What we did was just take the guts out of a regular
17 D cell and put them inside of the cell, and there is a little
18 tab hanging out and you weld it to the lid. It was on the
19 seal when we put it together.

20 STEINHAUER: This was a spiral?

21 MC HENRY: Yes.

22 STEINHAUER: It seemed like you had to get in between
23 the top of the spiral and the bottom of the cover.

24 MC HENRY: Well, what you do -- that is not a very
25 good schematic -- you bend the tab this way so it folds up like

1 an accordion when you put it together. I guess they pretty
2 well do that now when they put the lids on cans, anyway,
3 when they weld them up?

4 HENNIGAN: I would like to have Dr. Park of
5 Goddard Materials Group give some of the results of an analysis
6 of actual cells that we have used for spacegroup programs.

7 Dr. Park.

8 PARK: (Goddard) I would like to mention that
9 perhaps you really don't care to hear about what I am going
10 to talk about. We would have to call these failures.

11 There really aren't too many, which you may prefer,
12 but they are actual failures and this is sort of an example of
13 what we do because we are in the Materials Engineering Branch?

14 We are available for consultation and also for
15 failure analysis.

16 One of the examples that we received was a nickel-
17 cadmium six ampere-hour cell, numbered 149 and 151. Taking
18 it open, we got what is shown in the first slide.

19 (Slide.)

20 This was most interesting because of this area
21 right over in here where you see we have apparently loose
22 material coming off. We had been told this was a nickelplate.
23 This particular seal came out of the battery cell No. 151;
24 it was actually the positive electrode, and 151 had received
25 -- let's see, it was tested at 25 degrees C. to a 25 percent

1 depth of discharge.

2 Looking at Cell No. 149, we didn't see this at all
3 and yet Cell No. 149 was tested at 40 degrees C. to a 25
4 percent depth of discharge.

5 I might add we haven't opened many of these cells
6 but this, I presume, would be a potentially bad situation to
7 have in any of your cells.

8 One other example is shown in the next slide.

9 (Slide.)

10 This is from General Electric's 100 ampere-hour
11 cell. This looks extremely bad but it's the advantage of an
12 electronic scanning microscope that you can see such depth of
13 focus and this actually might be at about 250 magnification,
14 and yet a spot was visible without any magnification along
15 the brazed area.

16 Well, seeing a spot like this, you would like to
17 see how deep it is, but we also can look at it another way,
18 as shown in the next slide.

19 (Slide.)

20 This is X-ray penetration. As you may be aware,
21 there are a number of concentric circles of ceramic, of metal,
22 of holes, actually, and thus the X-rays pass through where
23 they can and in an area like this they pass through very
24 easily; we we concluded that this was the area of the hole.

25 The best way to look at that is to section it and to

1 try to grind down so that we could see how deep that hole goes.

2 As indicated in the previous slide, it didn't look
3 too bad and yet you cannot tell much from the surface, so, in
4 the next slide,

5 (Slide.)

6 you can see how long it did extend. This actually, up here,
7 is not quite at the edge of the material and as this goes
8 up farther and as we come down here you can see how long it is;
9 and the question is, does it continue any farther. For the
10 benefit of the G.E. people, I would have to say it probably
11 doesn't, and I think it ends about here in this area. While
12 this is a surface we cannot necessarily tell whether it goes to
13 the left or to the right, but it does appear as though a
14 short distance on we reach the end of this hole.

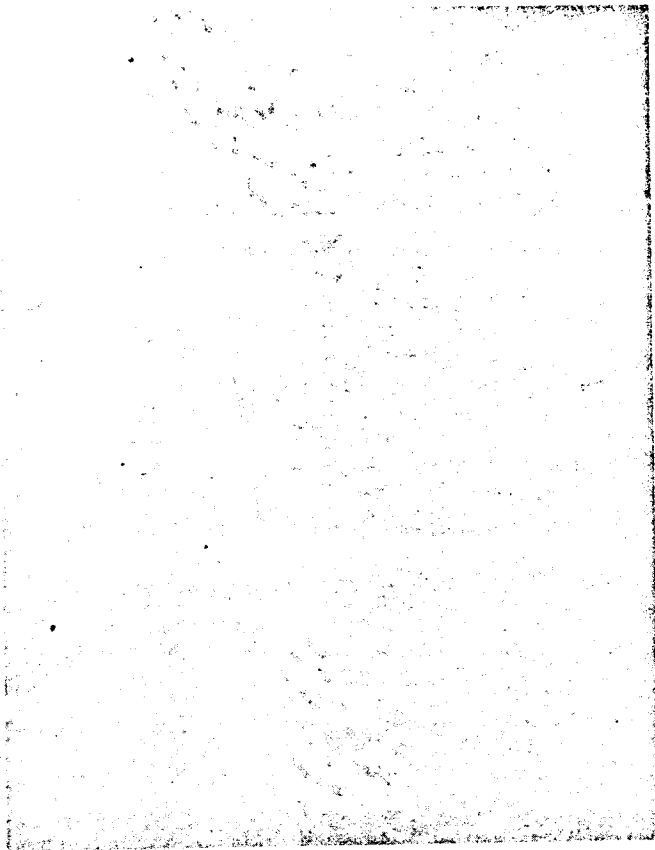
15 However, it is a good proportion of the total length
16 of the brazed area which is obviously not as they desired.

17 In the next case, this was from a Gulton battery,
18 serial No. 227; it was called an intermittent leaker. We had
19 a leak rate of 6.03 times 10 to the minus 8 standard cc's per
20 second, which doesn't sound bad at all.

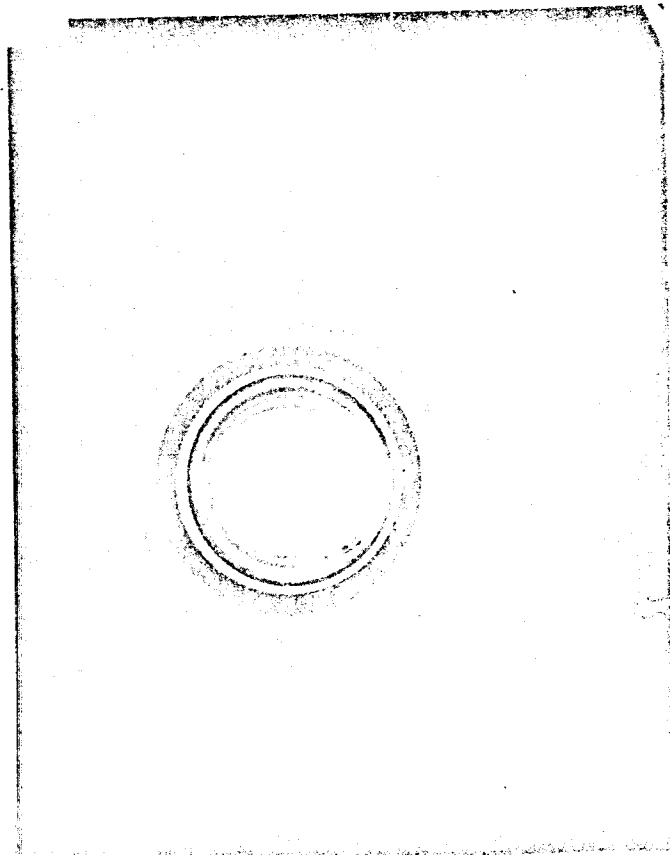
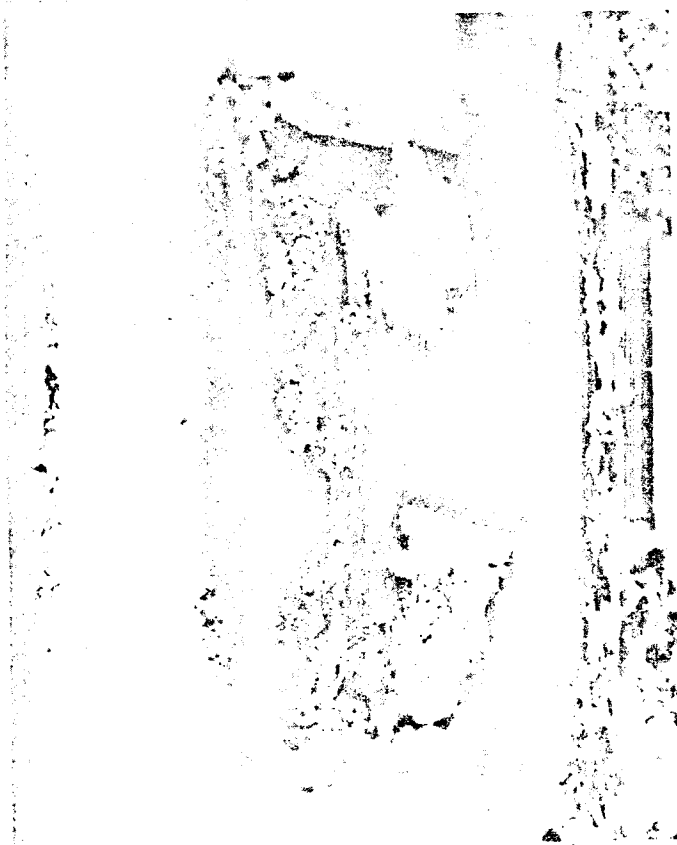
21 We could detect a leak when we had a differential
22 pressure of about 20 pounds of helium and thus we could look
23 for bubbles.

24 (Slide.)

25 In this slide you may have trouble finding where the



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1 hole is, but right in there. This is a relatively small area
2 but here again it was visible without magnification. This
3 magnification is on the order of 15X. Now here again we did
4 decide to section it and look deeper into this, and, in the
5 next slide

6 (Slide.)

7 it doesn't look bad, particularly up here. This is where the
8 hole had been and this is the brazed area, I might add, here.

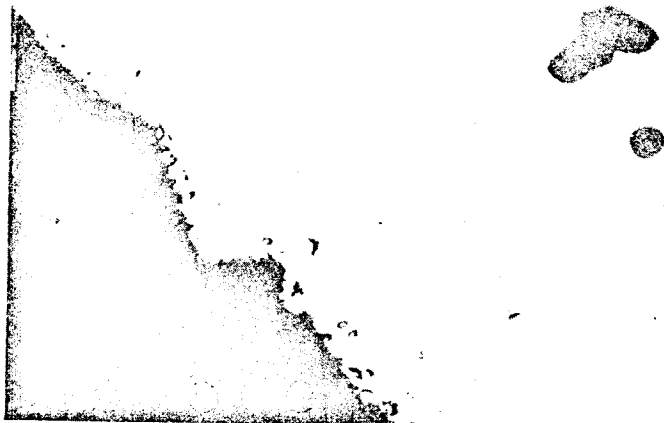
9 There is obviously a hole down here, maybe a gas
10 pocket and another one down here; but there is apparently no
11 continuous path from this point down into the cell. However,
12 in the next slide --

13 (Slide.)

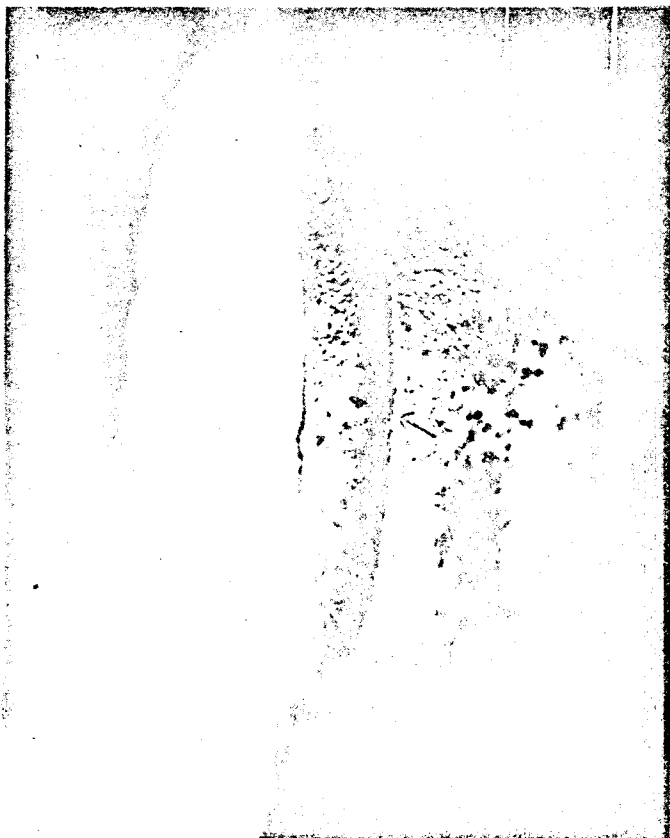
14 -- you can see that there is indeed a continuous leak path.
15 This is rather tortuous. For example, you have real good
16 gates all the way through to the outside and very possibly right
17 in here is where the actual leak did occur.

18 These really are the only bad examples I had of
19 possible failures and I would like to point out that, as I did
20 in describing them, these areas were visible to the naked eye;
21 they would be even more visible at say 20X or 40X, which isn't
22 very high. You don't need to go to a scanning electron
23 microscope to find them.

24 I might also add that the X-ray did indicate that
25 there was a very suspicious area and it is obviously easier to



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1 me if you find these suspicious areas before you have even put
2 them into a cell, you will be way ahead without having to go
3 through a life-cycle testing to find out that, yes, you did
4 have a leak.

5 Thank you.

6 (Applause.)

7 ENNIGAN: We have a question from Fred Betz.

8 BETZ: (Gulton) It is really on the order of a
9 comment. Both of those seals and the serial numbers of the
10 cells represent what I believe to be a design that has been
11 discontinued for about three years. We did recognize the
12 deficiency in the seal design; it has been corrected to
13 the design that Bob Steinhauer showed. There is one other
14 thing I wanted to mention but I forgot what it was.

15 These are quite early cells as far as the design.

16 PARK: Yes, that is very possible. It is encouraging
17 that once you can recognize this type of failure, why there is
18 a way of getting around it. And it is encouraging that these
19 have been changed or improved.

20 BETZ: I think the other factor was we do use
21 visual microscopic examination of our brazed joints on all of
22 our seals now.

23 PARK: Yes, I feel that that is a very good quality
24 assurance procedure to follow.

1 hole was very large, yet it did continue on into the cell
2 itself.

3 HENNIGAN: Are there any further questions?

4 Bob Steinhauer?

5 STEINHAUER: (Hughes) Perhaps Fred Betz answered
6 the question, but on your first slide, was that one of the
7 seals that Fred was referring to? You did not comment upon the
8 gray area moving up from the bottom along that ceramic as
9 being a possible failure.

10 PARK: No, I thought that was more the lighting of
11 the picture itself; it was more of an artifact.

12 BETZ: That was pure silver, I believe, with a
13 bright silver play, both of which have been discontinued.

14 HENNIGAN: There is time for one more question.

15 Sid Gross?

16 GROSS: (Boeing) We have tried to determine if we
17 can inspect ceramic seals with X-rays to detect flaws as a
18 screening method. It is very difficult to take X-rays because
19 of the geometry. However, if you really bend over backward
20 and take a number of X-rays at odd angles, you can do it.

21 The thing that we found is that you have not much
22 difficulty in finding defects in most of the seals that we
23 examined this way.

24 FORD: One point for clarification. The photograph
25 of the 100 amperé-hour seal that you are examining was never

1 put on a cell. It was provided before it was used.

2 HENNIGAN: We will break for lunch.

3 One more question. We have to make the cafeteria
4 by 1:00 o'clock.

5 Go ahead, Bill.

6 BILLERBECK (ComSat) I just wanted to ask if you
7 also found that this was a difficult procedure? Did your
8 experience correlate with Sid Gross' experience? It takes
9 X-ray photographs from various angles to be able to see these
10 failures.

11 PARK: I might add that we didn't have any real
12 problem in taking these. We did go through a -- let us say
13 five different kilovolt settings and let it go at that. We
14 picked out the best one and these were straight-on shots
15 and offered no real problem at all.

16 It may have been an advantage that we had cut cell
17 open and had been easy to get at, but this should normally
18 be carried out before they are put into a cell.

19 HENNIGAN: Any of the speakers for this afternoon,
20 I wonder if they would come down and talk to Bill Billerbeck
21 in the corner over here. Bill, stand up for a minute so
22 everybody can coordinate with him in the afternoon session.

23 Whereupon, at 12:55 p.m., the meeting was adjourned
24 to reconvene at 2:00 p.m. this same day.)

5 Session 4 - NEW DEVELOPMENTS - W. BILLERBECK, CHAIRMAN
0

1 AFTERNOON SESSION

N71-28674
(2:00 p.m.)

2 HALPERT: Can we take our seats, please, and start
3 the afternoon session.

4 We plan to go into our fourth session and at the
5 end of this fourth session, after completing the work on new
6 devices, we will try and then summarize some of the work that
7 we have accomplished here today and maybe list some of the items
8 that we ought to be doing in the future in order to bring
9 about a more reliable system.

10 So, at this time, I would like to introduce our
11 chairman for the fourth session, Bill Billerbeck, who is
12 Manager of the Electric Power Branch at COMSAT Labs and the
13 gentleman who is chairing the Specifications Committee for the
14 high reliability nickel-cadmium cells.

15 I present to you Bill Billerbeck.

16 BILLERBECK: Thank you, Gerry. Good afternoon,
17 gentlemen. This session is entitled "New Developments." I
18 guess that means that we are up with the present state of the
19 art of nickel-cadmium cells.

20 We have been through all that in the last couple of
21 days, so we are going to try to have a series of relatively
22 short presentations on new technology, new test techniques,
23 new developments in nickel-cadmium cell technology and advanced
24 energy storage techniques.

25 I thought that Chuck McKenzie's keynote speech that

1 we had at the start of this meeting was particularly appropriate
2 in pointing out that the requirements for aerospace batteries
3 have been changing considerably in the last couple of years.
4 We still have some of the experimental, short-life type of
5 spacecraft with us but we also have some other needs.

6 One of these is this need for much longer life, the
7 order of five or ten years. In many cases it is principally
8 in the storage mode with perhaps a few deep cycles a year, like
9 100 cycles.

10 These requirements stem from the application-type
11 spacecraft in synchronous orbits, used for communication,
12 navigation, meteorology and earth resources. We also have the
13 long interplanetary missions, those requirements now.

14 So I want to point out that these are becoming a
15 larger portion of the aerospace battery business at this point
16 in time and so much more work is needed to understand and
17 improve the performance of the ni-cad cell under these conditions.

18 I think this afternoon we have several interesting
19 papers on testing devices that will help us in this area to
20 understand cell performance.

21 Looking further ahead, I think another need that is
22 becoming more important is the need for improvements in energy
23 density, and I think that one can say that there is a need for
24 improvement in the ni-cad cell performance, and I think we can
25 go quite a long ways there in energy density; and also in

jrs 3

1 couples with higher energy density capability. We we have
2 several papers this afternoon on silver-zinc and possibly a
3 paper on zinc-air.

4 Then, just recapping for a second, the two papers
5 on test techniques are Bill Webster of NASA, Goddard; Jim
6 Stemmler of NASA, Goddard; and we have Dr. Reed from Battelle
7 on a plaque structure for nickel-cad; and then we have Bill
8 Nagle from NASA-Lewis Lab on silver-zinc; Dr. Mikkelsen from
9 General Dynamics on silver-zinc and Tom Hennigan on automatical-
10 ly activated silver-zinc.

11 Those are the papers and without further introduction,
12 I would like to ask Bill Webster to give his presentation.

13 WEBSTER: (NASA, Goddard) Thank you very much.

14 One of the disadvantages of being the host is
15 sometimes your boss volunteers you for talks before the work is
16 completed, so this is really an interim report on some work
17 that is currently underway and Tom thought that it might be nice,
18 since we just had our first results come in, to make you aware
19 of what we are doing and possibly if it is of interest to you
20 then we can give you some hints to accelerate this application
21 for your own use.

22 What we are doing is looking at strain gages as a
23 technique for monitoring pressure in a cell. Quite a bit of
24 work has been done and most of the absolute measurements have
25 been made with pressure transducers, but spacecraft managers

1 here at Goddard and possibly in private industry don't buy the
2 concept of flying a \$350 pressure transducer on top of a cell.
3 Also, this pressure transducer is usually attached by a
4 mechanical means through a fill tube which is structurally a
5 very poor mode of attachment.

6 These pressure transducers are bulky and they are
7 expensive.

8 The other type of pressure measurement that most
9 people are familiar with is the adhydrode or signal electrode.
10 This is mounted internal to a cell and is used to sense
11 oxygen pressure. It is not an absolute measurement of oxygen
12 pressure but just an indication and at low pressures is an
13 excellent indicator.

14 The other disadvantage of this type of electrode
15 is that in a flooded cell it does not work or in a wet cell,
16 not necessarily flooded but wet, I am doing some research right
17 now with calorimetry and my first 100 ampere-hour cell that I
18 have been playing around with has such a signal electrode in it.

19 In order to get good transfer between these large
20 plates, more electrolyte than usual is used. The third
21 electrode in this particular case is not working, oxygen is
22 being generated and the rate of diffusion for this electrode
23 is extremely slow, so that you are many hours behind what is
24 actually occurring in the cell.

1 gages as far back as 1967 and it has been the type of effort
2 where it has cost the government only our time and only when
3 we can spare it, which is becoming less and less.

4 What we are doing is using a wheatstone bridge
5 circuit in which the opposing legs of the wheatstone bridge
6 are the strain gages which measure the strain on the bottom of
7 the cell. The other two legs of the wheatstone bridge are
8 strain gages mounted on a metal tab which is welded to the
9 bottom of the cell. These two are to serve as a temperature
10 compensating loop of this circuit.

11 (Slide)

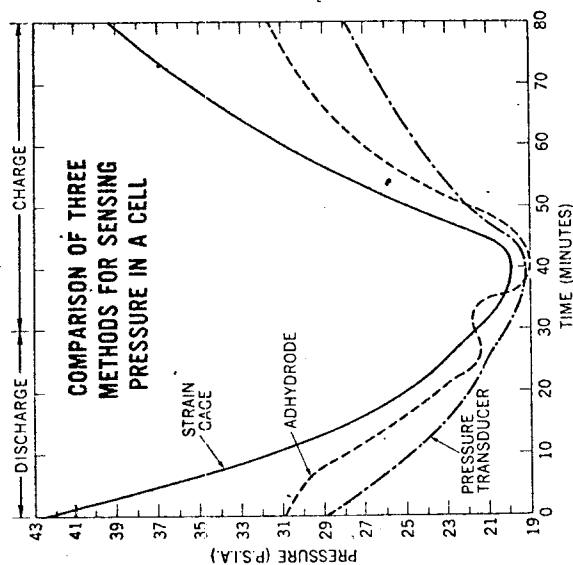
12 This is a crude drawing of the bottom of a 20 ampere-
13 hour cell. These two strain gages located in the center of the
14 cell will measure the actual strain that the bottom experiences
15 when pressure is generated.

16 Right here is a well with a similar metal, same type
17 of stainless steel, with two strain gages over here for the
18 temperature compensating loop.

19 Our first trick that we discovered was that if you
20 take two opposing legs of the wheatstone bridge and you use this
21 for your strain gages you can double the output signal.

22 The next thing that crossed our mind was that most
23 20 ampere-hour cells for instance are comprised of 30 mill

24



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1 thick stainless steel. And I asked myself and a mechanical
2 engineer why. We couldn't come up with any good reason why.

3 We found out through some preliminary calculations
4 by this gentleman that we could easily go to half this thickness
5 and have a safety factor of at least threefold for pressures
6 over 100 pounds.

7 So our next idea was to take the bottom of the cell
8 and have the thickness of the metal on the bottom be half that
9 of the rest of the cell, typically 15 mill. So we let a
10 contract to Gulton Industries in 1968 to build us, oh, about
11 half a dozen cells; and at that time they only had material
12 available which was 19 mills thick, so we ended up with one-
13 third as thick.

14 Well, then we let a contract in the nature of \$5,000
15 to NBS Mechanical Systems Group to apply strain gages to the
16 bottom of this cell and to do the wiring for us and apply the
17 best techniques known so we wouldn't have to worry about
18 training chemists and engineers to do something which is already
19 known.

20 The results that they found comparing a standard
21 cell versus a cell where the bottom was one-third thinner was
22 that we were again able to increase the output of the strain
23 gage circuit by a factor of 3; so by using two strain gages as
24 opposing legs we can double it by using one-third thinner we

1 can triple the signal.

2 The reason why I am so concerned about increasing
3 the strength of the signal, is that this signal is extremely
4 low. It is in the order originally of 1 to 10 millivolts.

5 So, the next thing we inquired into was how do we
6 get this back to earth? Does the electronics already exist?
7 Of course, the answer is yes. People have been using strain
8 gages for a long time.

9 We found out that there is a small space-qualified
10 box approximately two inches square by one inch thick which
11 acts as an exciter amplifier and it can excite a strain gage
12 circuit and amplify the signal by a factor of a thousand. So
13 now we are talking about sending back signals on the order of a
14 volt.

15 Recently we received these cells back from the
16 National Bureau of Standards and we have put them on test here
17 in our laboratory. We have done a very minimal number of tests
18 to this point. It consists of several conditioning charges
19 at C over 10 for 16 hours and then one which we call typical
20 OAO experiment.

21 Now the results of our 16 hour charge were figures
22 like the following: The adhydrode signal over 16 hours for
23 a dead-shortcd cell at the end of one minute was reading
24 47 millivolts; at the end of five minutes, 37; at the end of
25 200 minutes, 29. So the adhydrode wasn't tracking the pressure.

Then at the end of 960 minutes, which is representative of the 16 hours or equated to 16 hours, was 455 millivolts.

I spoke to Mr. Ford about this and he said this is common when you are working with a dead-short cell and starting it up for the first time, and he associates it with a certain activation of the electrodes involved.

The pressure transducers during the same time was very linear in responses as would be expected and it went from 51 millivolts to 82 millivolts, never decreasing or fluctuating.

The strain gage output ran from 7 millivolts to 12 millivolts, so you can see we are talking about extremely small. They were extremely linear, never varying with time as a result of fluctuations in temperature.

These experiments were conducted at 20 degrees C.

Then we initiated what we call an OAO test regime. In this regime we charged at 12 amps to a voltage clamp of 147; then allowed the current to taper. We discharged at 6 amps for 30 minutes. This type of regime gave us 155 percent overcharge.

Now, we are not recommending this for all OAO but we are trying to measure the pressure, so that is what we were about, by having such a high overcharge.

We have also done other experiments where we have upped this voltage limit to 149; then we are talking about 200 percent overcharge.

The only data I had time to reduce for this meeting

1 was this experiment with the voltage limit of 147 and an
2 overcharge of 155 percent.

3 (Slide.)

4 Here we have a slide of that data for the 100th
5 cycle. This was conducted at room temp -- well, not exactly
6 room temperature -- in a temperature chamber at 20 degrees C.

7 This is a typical computer printout of the data and
8 factors have been applied to the data. But you can see that
9 in the 100th cycle we had a 90 minute orbit, 30 minutes of
10 discharge and 60 charge.

11 We started out first with our discharge and then we
12 go into our charge. Our baseline should be the pressure
13 transducer; that is an absolute measurement. We are coming
14 down off of the last end of overcharge at 29 pounds of pressure
15 and dropping down by 10 minutes into the charge to approximately
16 19 pounds of pressure and then swinging on up.

17 The next curve I call your attention to is the
18 adhydrode. The adhydrode also follows the pressure. This
19 little whiffle in the curve at 30 minutes is where you change
20 from charge to discharge. Because we can only plot versus one
21 axis a number had to be multiplied by the millivolt output of
22 the adhydrode and this makes this curve appear a little bit
23 smoother than it really occurs. It is a sharper break than
24 if you are just monitoring straight millivolt output, but you
25 can see it also follows.

1 Then we come to the strain gage and we have a
2 perfect profile of the pressure in the cell. What are these
3 numbers and what were they multiplied by? In this particular
4 cycle, the pressure transducer went from 75 millivolts to 115
5 millivolts and it was multiplied by a factor of 240.

6 The adhydrode had a swing from 310 millivolts to
7 516 millivolts and it was multiplied by a factor of 61.

8 The strain gage had a swing from 8 to 18 millivolts
9 and was multiplied by 23,750. The voltages that the cell was
10 experiencing at this time was a low of 126 to a high of 147,

11 So, what we are talking about in translating some of
12 this into absolute values, is the strain gage delta was 10
13 millivolts, the pressure transducer was 40 millivolts and the
14 adhydrode was 200 millivolts.

15 What we are proposing for the future is to construct
16 a cell in which the bottom has a small area which has been
17 milled down to a thickness of approximately 10 mills. This
18 would be a small circle into which was placed the strain gages.
19 What this would do would actually make the entire cell case act
20 as a pressure transducer and would further enhance this output
21 and would give us a reproducible surface.

22 We have not had time to analyze this data but there
23 are two obvious problems that I can see right now. One would
24 be of application, which technician put on strain gages on which
25 day? So it would be very expensive to calibrate each single

1 cell.

2 The other possible trouble spot would be that you
3 had different welders and different stresses put on the bottom
4 of each cell when it was constructed; but we feel by making
5 this sort of pressure transducer out of the case and having a
6 small area of a thinner construction than the rest of the
7 bottom, that we can eliminate any hysteresis due from one
8 welding application of one day to that of another day, and
9 this pretty much is the state of our work at this time in this
10 area.

11 (Applause.)

12 BILLERBECK: Do we have any questions?

13 STEINHAUER: (Hughes) Bill, is there any particular
14 reason why the bottom of the cell was selected particularly if
15 the silent cell was open and you could put your thinned out
16 area midway along the side away from the weld areas?

17 WEBSTER: Thank you, Bob, for calling that to my
18 attention. Yes, there was.

19 We turned this cell over originally to a group here
20 at Goddard which put a particular light-sensitive material on
21 the cell and then applied high pressure to the cell and then
22 analyzed the cell for the area of greatest stress and most
23 uniform stress. That was at the bottom, so that is why it was
24 selected.

25 BILLERBECK: Other questions?

1 All right. Thank you very much, Bill.

2 The next paper that we have is by Jim Stemmler from
3 NASA, Goddard, and it is on sealable experimental cell case
4 for nickel cadmium cells, and perhaps other uses, too.

5 STEMMLE: (Goddard) Thank you.

6 I envision this as a rather short talk. In fact I
7 got into an argument with Gerry Halpert. Initially I thought
8 I would talk 15 minutes but then when I looked at what I had
9 to talk about I said five and he said no, you had better take
10 ten. So I guess we will just have to see.

11 Suppose your job description says you are a
12 research electrochemist and one day you hear somebody say
13 something like if you put carbonate in the electrolyte, it
14 advances the onset of gasing of the nickel electrode or some
15 such thing as that. Wouldn't it be nice if you could go into
16 the shelf in your laboratory and pick off the shelf something
17 like this?

18 (Slide.)

19 This is a resealable convenience experimental cell.
20 We thought it would be nice, so we designed one. The features
21 that this thing has are, one, it is flexible. If you notice
22 in the top, and it will show up more clearly on later slides,
23 there are six ceramic terminals, two of them for carrying a lot
24 of current and four for carrying signals of various sorts for
25 monitoring what is going on in the cell.

1 The advantages of this thing are that, one, it has
2 this flexibility, it is sealable, it can measure pressures,
3 it can measure gasing characteristics; and, two, there is a
4 cost reduction. Each time you want to make a cell you don't
5 have to make an entirely new cell which you seal off and weld
6 off and have to discard when you tear into it.

7 (Slide.)

8 Here is a picture of the header. There is a pipe
9 coming out and the threads are 1/8" pipe. You can see clearly
10 the two large current-carrying electrodes and the four smaller
11 signal electrodes.

12 (Slide.)

13 The third slide is the reverse of this, showing the
14 foot that we designed for attaching to current-carrying
15 electrodes and the electrical connection to the auxiliary
16 electrodes, coming out of their ports.

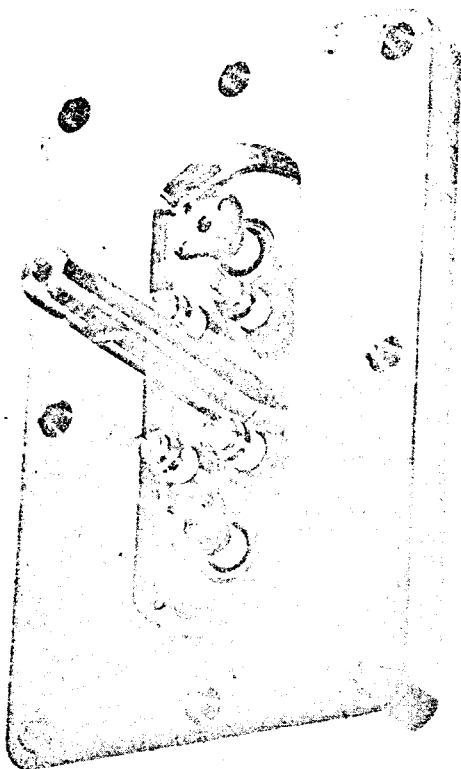
17 (Slide.)

18 The fourth slide shows the O-ring seal. The
19 quarter there is not really a measure of how much it cost; it
20 is to give you an idea of how big it is.

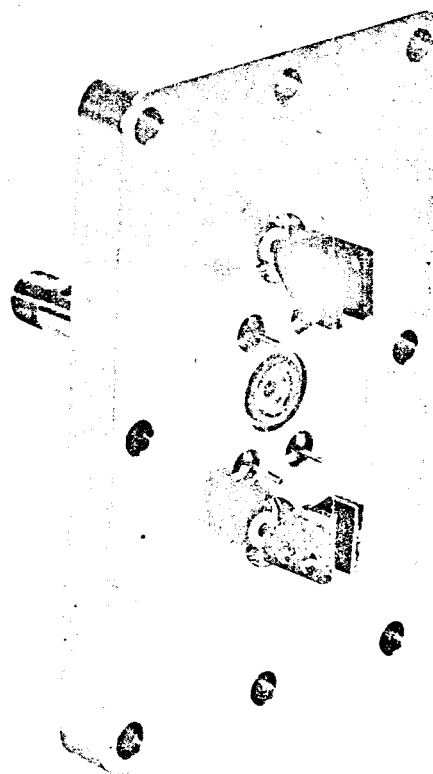
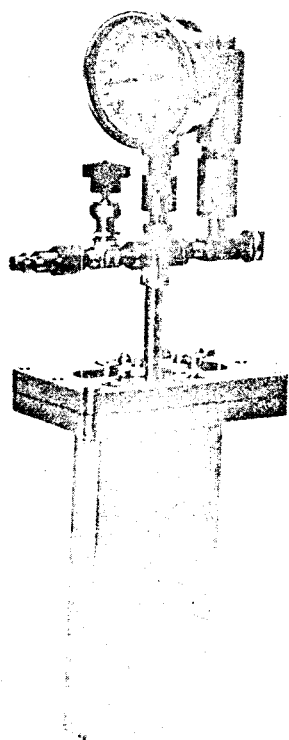
21 The O-ring which we bought was made of ethylene
22 propylene which is resistant to KOH, according to the Parker
23 Hanniford Company.

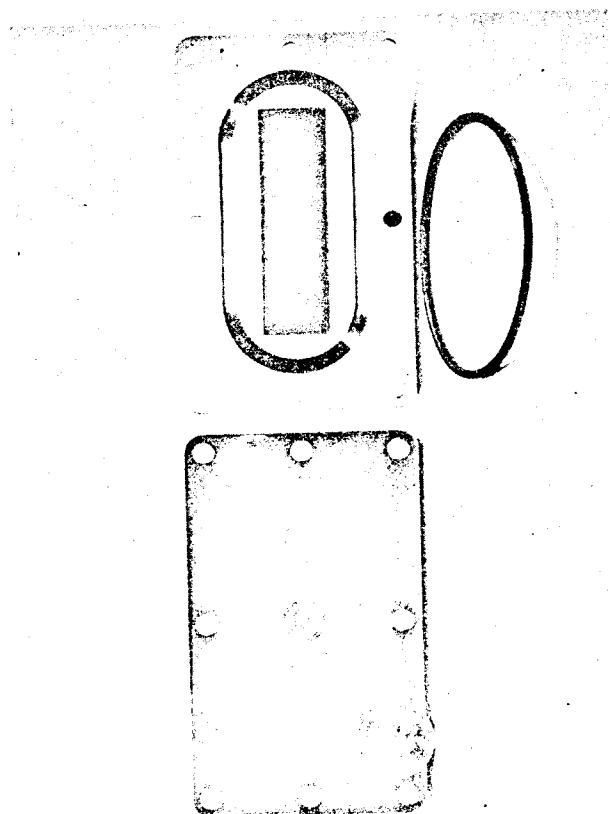
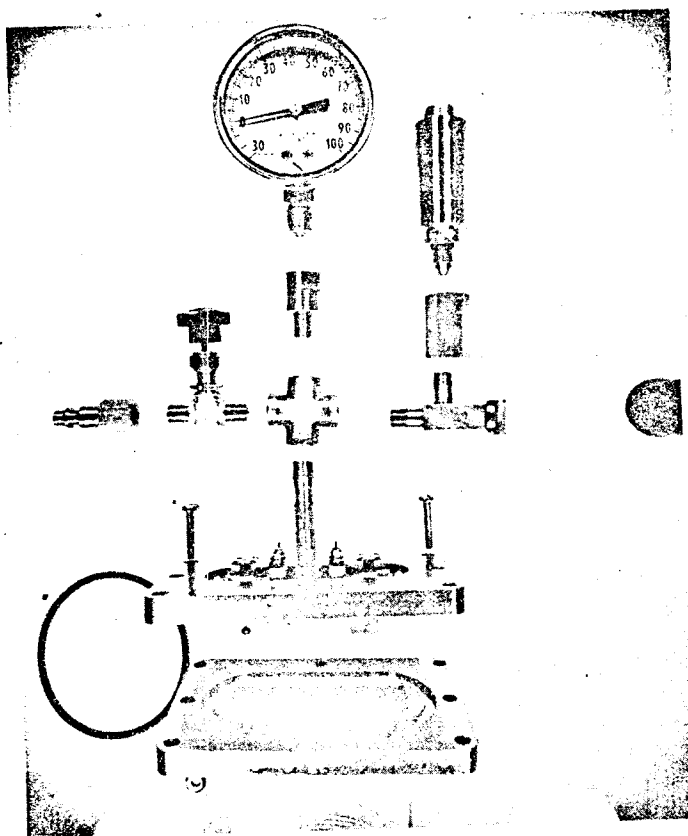
24 (Slide.)

25 In the next slide we see an exploded view of the



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1 convenience manifold. We have a gage, a pressure transducer, --
2 let me see if I can point to these things -- we have a gas
3 sampling manifold there of Goddard's own design, a valve quick
4 disconnect fitting, and a pipe tee. The top and bottom are
5 just held together by machine screws.

6 The cost of the cell case, exclusive of the manifold
7 is about \$565. The material could be either nickel or stainless
8 steel. When we had these made there was a nickel strike so we
9 had it made out of stainless steel, out of 304-L.

10 We also had at the same times some shims made so
11 that you don't have to use an entire plate stack; this thing
12 will hold a 20 ampere-hour plate stack, but you could do
13 experiments on fewer electrodes than that and use shims to
14 occupy the void volume.

15 We have run into some problems, probably not where
16 you would expect to run into them. We have developed some
17 leaks in the bottom edges of the can.

18 We had two or three leaks right on the corner. When
19 I took it to a man to see where it was leaking, he told me it
20 was going to be leaking around the ceramic seals but it wasn't.

21 The design is good. We have on hand about ten cells
22 that have been holding 50 pounds of air for a month or so,
23 just not dropping, so the design is good.

24 We also designed a small device for connecting
25 signal electrodes to the feed-throughs. Maybe I will just try

1 drawing one. It is simple enough that way. There is a hole
2 going through here. There is a set screw going through here.
3 Simple enough. We intend to weld the leads onto this metal
4 and then fit this over the feed-through and tighten it down
5 with set screws.

6 That is all I have to say, and I wonder if it was
7 five or ten minutes?

8 (Applause.)

9 BILLERBECK: Do we have some questions on Mr.
10 Stemmler's paper?

11 All right, if not, we will go on to Dr. Alan Reed
12 from Battelle, and he is going to tell us about a new
13 honeycomb plaque structure for nickel-cadmium electrodes.

14 I guess I had better give Jim back his baby here.

15 REED: I have just one that might be a Viewgraph --
16 not a Viewgraph but the overhead projector.

17
18 We at Battelle have developed a new type of porous
19 nickel plaque that we made into cadmium electrodes. I might
20 add that this has been developed on contract here with NASA,
21 Goddard.

22 These plaques have a honeycomb structure and they are
23 made by alternately stacking thin, electroformed, corrugated
24 nickel foils and flat nickel foils. The foils are bonded in a
25 hydrogen furnace and then they are sliced into plaques of the

:XXXX

1 desired thickness; for example, 30 mills.

2 If I could have that overhead, it will show you a
3 cross-section.

4 (Slide.)

5 This has been filled with epoxy and sectioned.
6 You will see that all the pores are uniform in size and shape,
7 triangular; they are parallel to one another and each is
8 connected directly to the surface of the plaque providing the
9 straight-through pore.

10 I think that is probably enough for the slide.

11 Lights, please.

12 We made these plaques with five different sizes of
13 pores and the widest dimension of the pore in these various
14 plaques that we have made ranged from 3.2 up to 10 mills,
15 which is about a factor of 5 to 20 greater than the median
16 pore diameter of a sintered powder plaque. Therefore the
17 internal surface area of these plaques is much smaller than that
18 of a sintered powder plaque, ranging from about .04 square
19 meters per gram up to about .1 square meters per gram compared
20 to one-quarter to one-half a square meter per gram for
21 conventional sintered powder plaques.

22 We have developed some new technology in making
23 these thin foils because we had to electroform pinhole free
24 nickel foils as thin as about 2/10ths of a mill. This work
25 involves careful preparation of machined mandrels with evenly

1 spaced grooves onto which we electroformed the thin nickel
2 foils and then stripped them off.

3 We described this work in a report that will be
4 soon coming out under contract NAS5-21105.

5 When these plaques are made into cadmium electrodes
6 they have charge and discharge curves which are very similar
7 to that of the conventional sintered powder plaques, in that
8 one obtains a relatively flat charge and discharge plateau when
9 measured versus the reference electrode.

10 We believe that this shows that the high internal
11 surface area plaque is not necessarily for proper electrode
12 performance; rather, the cadmium in the electrode forms its own
13 high surface area, the little crystals of cadmium.

14 I have a photograph of one of these impregnated with
15 cadmium. It wouldn't show up on this Viewgraph but it looks
16 almost like sand packed into the end of these open pores.

17 We have also found that this charge-discharge
18 performance is relatively insensitive to the size of the pores
19 that we have made.

20 The whole purpose of this work was to build longlife
21 electrodes by providing a porous structure which intuitively
22 one thinks is more or less the ideal structure for porous
23 electrodes. That is, all of the pores are of uniform size and
24 they all are parallel connecting directly to the surface of the
25 electrode. This design should help to maintain uniform current

1 density and thus promote long life.

2 One of the pore sizes of these honeycomb electrodes
3 did show a better performance as far as utilization goes than
4 did the others. These plaques had a capacity of about 200
5 milliamp hours per square inch at the one hour rate compared
6 to 280 milliamp hours per square inch for a sintered powder
7 plaque operated at the same rate.

8 I believe, though, that by modifying or impregnation
9 process we could increase the capacity of these honeycomb
10 electrodes to a point where it is equivalent to a sintered
11 powder plaque.

12 I will say why I think that now. When these plaques
13 were impregnated with the standard vacuum cadmium nitrate
14 process they were found to require between two and three times
15 as many impregnation cycles as were required for sintered
16 powder plaques to reach the same loading of active material
17 based on weight gain.

18 After we impregnated these to that point, they were
19 analyzed chemically for cadmium and cadmium hydroxide and this
20 analysis showed that a major portion of the impregnated
21 active material was metallic cadmium, rather than cadmium
22 hydroxide, as is found with sintered powder plaques.

23 Thus the electrochemical utilization ranged only
24 from about 40 to 60 percent of the theoretical capacity compared
25 to greater than 70 percent with the sintered powder plaques.

1 It seems that the normal nitrate impregnation
2 procedure must require some modification for these open
3 honeycomb plaque structures. Perhaps either the time of
4 polarization or the current or both should be decreased to
5 reduce the amount of active material which is reduced to
6 metallic cadmium, since it appears that the large amount of
7 reduced metal in these ne plaques may have resulted in the lower
8 utilization.

9 We stayed with this impregnation procedure though
10 because we had decided earlier in the program that we did not
11 want to change our impregnation procedure and thus have another
12 variable in the process.

13 In summary, this work shows that plaques can be
14 made with the uniform non-interacting pore structure and that
15 such plaques do function similarly to normal sinter powder
16 cadmium electrodes.

17 More work needs to be done to optimize the
18 impregnation procedure and perhaps some electrochemical
19 processes described yesterday might be tried with these.
20 But because we have found good initial performance and because
21 these plaques have the structure one intuitively believes
22 an ideal plaque should have, we believe there is justification
23 for continuing this work and one of the next things that should
24 be done is to build nickel-positive electrodes from these
25 plaques also; and then test them in sealed cell operating

1 conditions.

2 Thank you.

3 (Applause.)

4 BILLERBECK: Haven we some questions on this paper?

5 COHN: (NASA) I have a couple of questions.

6 One of them, you, apparently like everyone else, has striven
7 to load as much active material into the plaques as you
8 possibly can.

9 Is there reason to believe why one should try to
10 load the plaques as highly as possible when we only use about
11 20 percent or so of the loading?

12 REED: Actually this wasn't the original goal. We
13 have striven to obtain a 40 percent of the pore volume filled
14 with cadmium hydroxide based on the weight gain and we used
15 sintered powder plaques as controls and as I said when we
16 analyzed these we found about 90 percent of this weight gain
17 in the sintered powder plaques was cadmium hydroxide.

18 Now then we were going on this assumption that it
19 was also cadmium hydroxide in the honeycomb plaques so we wanted
20 the weight gain to be equivalent to what would be 40 percent
21 filling of cadmium hydroxide. So we erred and got more loading
22 of active material as cadmium than we originally had hoped for.

23 So I think you have a very good point about not
24 overloading these. Our goal was 40 percent as cadmium hydroxide.

25 COHN: The other question which is somewhat related

1 to this is, have you made some provision for the expansion
2 and contraction that takes place when these electrodes are
3 charged and discharged, so that you don't apply any undue
4 stress to them as they are used?

5 REED: I am not sure whether the inherent structure
6 of these would take up that motion or not. This is another
7 reason for not loading too heavily so that they would not
8 break.

9 The plaques are considerably stronger physically
10 than a sintered powder plaque. You know if you take a sintered
11 powder plaque and curl it around a small radius, even if it is
12 a good sintered plaque it still cracks. There is no question
13 about that. These can be curled around a radius as small as
14 1/8" making a loop out of them, either in the direction
15 perpendicular to the bonds or parallel to the bonds without
16 breaking.

17 DUNLOP: (COMSAT) I have a couple of questions, too.
18 What was the density of your plates? I didn't
19 catch that.

20 REED: I guess I didn't mention that, but you mean
21 the porosity?

22 No, the density -- well, I want to know if
23 you had a term in terms of grams per cubic inch or something
24 like that.

25 REED: I cannot give you that figure but they were

1 80 percent plus or minus about 3 porous. The foils were
2 electroformed to the thickness required to maintain this
3 porosity.

4 DUNLOP: When you impregnated your plaque, what was
5 the percent by weight of the material that you impregnated
6 with to the plaque structure?

7 REED: It would have been about 50 percent of the
8 weight.

9 DUNLOP: About 50 percent. Was this -- how much of
10 the material could you utilize?

11 REED: It depended on the various runs. We utilized
12 from 30 to about 60 percent of this material based on the
13 theoretical capacity of cadmium analysis.

14 DUNLOP: Did you determine that the problem was one
15 of charging? Or was it a problem of discharging?

16 REED: I don't know. I think it might have been
17 both. When we started out they could be charged and discharged
18 almost 100 percent efficiently there, so I think whether you
19 want to say the problem was charging or discharging, I am not
20 sure. But the amount of material that was charged before
21 reaching the hydrogen-free capacity could be discharged.

22 DUNLOP: Thank you.

23 WILL: (G.E.) You have succeeded to provide
24 substrate which has parallel macropores; however, let's not
25 overlook that within this system of macropores you are still left

1 with the micropore system which is as tortuous in its paths
2 as in other battery plates, and I think an ideal structure would
3 consist in one in which one would have parallel micropores.

4 I have a question in addition to this comment.

5 I would expect limitations to this kind of structure
6 when you have considerable diameters of your macropores, like
7 up to 1.0 mills; I would expect those limitations to show up in
8 high rate charges and discharges, and I wonder to which extent
9 you have checked this part?

10 REED: We have charged these as high as 4 C rate
11 and discharged them also at this rate. Regarding your comment
12 about the size of the pores; this is true. They are considerably
13 larger than what you have in the microporous structure; however,
14 it also forms shall we say a cage for the active materials so
15 that the active material which you put in one pore must remain
16 there or move directly out into the separator rather than
17 sintering its way down -- sintering may not be the right word --
18 shifting down and packing in more tightly into other pores,
19 which is one hypothesis of reason for loss of cadmium capacity.

20 BEAUCHAMP: (BTL) I wasn't clear, what direction did
21 your pores run in the plate?

22 REED: The pores run perpendicular to the separator,
23 is that what you mean?

24 BILLERBECK: Any other questions.

25 Thank you very much.

1 BILLERBECK: Oh, one more question.

2 WILL (G.E.) It is surprising that your plates,
3 in fact, have such a high life capability. I would suspect
4 that this is due to the fact that your utilization is so
5 small and that you have considerable excess of cadmium in
6 there which accounts for that high rate capability and if you
7 were to go to higher degrees of utilization that in fact you
8 would run into a recommendation.

9 REED: That could be but the interesting thing about
10 these is that the capacity at the high rate did not drop off
11 significantly from the capacity at C and even down as far as
12 C over 4 rate.

13 The coulombic capacity was not greatly influenced
14 by the rate.

15 MAURER: (BTL) I was going to say something along
16 the line of Fritz here and suggest that part of this may be
17 that you really have is something akin to a pocket plate
18 electrode within the pore and what you have is a conducting
19 network of cadmium lacing the cadmium hydroxide and the low
20 utilization is simply the active material that is within these
21 micropores of the cadmium structure.

22 Ed McHenry of BTL presented some work sometime ago
23 on an electrode that was composed simply of cadmium oxide
24 powder and nickel flake or cadmium oxide powder and copper oxide

1 powder. In this case you get a micropore structure of either
2 cadmium or copper, depending on the materials and this gives
3 good, high rate performance and I suspect that that may be
4 part of what you have here.

5 One of the things that will really tell the story
6 is when you try to do this on positive electrode where you
7 don't get this type of action with nickel hydroxide.

8 If you can make a nickel hydroxide electrode with
9 these plates that has high performance characteristics, then
10 you are in, and if not, then this other mechanism may be the
11 important one.

12 If you try the electrochemical process, and I
13 encourage you to do so, you may get poor results if this
14 microporous argument holds because in this case in the
15 electrochemical impregnation technique you will only coat the
16 walls of these pores and not the center area; so you may have
17 high utilization but low total capacity.

18 REED: Regarding this electrochemical utilization,
19 If I could ask Dr. Maurer a question; he mentioned doing his
20 electrochemical utilization or his colleague mentioned it,
21 doing it in two steps or repeating it to get more material in.

22 What would you think of doing this to these types
23 of plaques to get a greater capacity? Do you see an advantage
24 in that?

25 MAURER: Well, I will pass this back to Beauchamp

1 but I would suspect that you would get gradually increasing
2 amounts of material, all right. I would be suspicious that the
3 utilization might drop in this case if the pores became very
4 full.

5 FLEISCHER: What is the thickness of the pores?

6 REED: 30 mills.

7 BILLERBECK: Any other questions?

8 Thank you very much.

9 Now we will change our order of speakers here, if
10 we can, please, and next have Dr. Mikkelson of General
11 Dynamics. I understand he has another engagement later on this
12 afternoon so we would like to get him up here now.

13 He is going to talk about silver-zinc storage
14 cells.

15 MIKKELSON: (General Dynamics) I would like to
16 thank Mr. Billerbeck for the honorary degree there. It is
17 just Mr. Mikkelson, and I would like to thank you for revising
18 your schedule, too. It seems that if you are near ETR and
19 they need someone at ETR they will send for you and they will
20 find you, so I have to make a little detour tonight.

21 I am a battery user rather than a battery designer
22 or a battery tester, per se, so my remarks are user oriented
23 and silver-zinc oriented because on the Atlas and Centaur
24 programs which I have worked on for about the last ten years
25 that happens to be the type of battery that we have used because

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1 it lends itself to our program more readily than a nickel-
2 cadmium or a silver-cadmium.

3 Briefly, I will describe how we use these to give
4 you a little background into some of the problems that we
5 do encounter from the user's side.

6 These silver-zinc cells or batteries -- we buy a
7 complete battery when we procure one, we don't assemble one --
8 come in the dry state and we activate them, usually one to two
9 days before a launch. Then we load test them in the laboratory.

10 The load test is usually very short because ampere-
11 hour-wise they are tailored to the missile's needs so you
12 cannot take too much capacity out of the battery in the labora-
13 tory. Usually we run a load test that is comparable to what
14 we feel the vehicle load is or what we know the vehicle load
15 is and then we check at the maximum specified rate to see if
16 the battery is still meeting its specifications.

17 Recently I ran into a problem where during the
18 running of this higher rate load test my battery voltages were
19 lower than they should have been. In investigating, I found
20 that these batteries had all been on the shelf in the area close
21 to two years and what was happening, apparently some loss in
22 silver-peroxide had occurred and possibly, according to some
23 of the battery vendors that I had talked to, some film had
24 built up on the plates.

25 The loss of silver-peroxide we were able to confirm

Tape 3
ending

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1 by recharging and discharging the batteries again. I could
2 never confirm the other theory that was put forth.

3 In order to solve this sort of a problem, I thought
4 about and have approached battery vendors with the idea of
5 taking a battery say after it is a year old and arbitrarily
6 activating it and discharging it and then recharging it, using
7 it for flight.

8 It has been our policy never to use recharged
9 batteries on flights for several years. They have come back and
10 one vendor said yes, this was agreeable, that it could be
11 discharged-recharged and be used for flight; and in fact we
12 had discussed the extension of life to the battery as we
13 presently use it has a 15 day life under ambient conditions
14 and a 30 day life if you store it at a lower temperature. He
15 is agreeable to going to 45 days.

16 One of the other battery vendors I contacted didn't
17 feel that he could to along with this because he felt due to
18 his separator design he didn't know enough about what might
19 happen to it and as a consequence he didn't have a great deal
20 of confidence in this type of a program, that two separators
21 are different in design. The vendor then indicated that he
22 could go along with it, as a U-type fold where you don't have
23 any exposed edges, and the other vendor happened to have an
24 S-type fold where you have exposed edges.

25 My purpose in recounting a little event like this is

1 that if we had been real smart in the beginning, we probably
2 would not have to be going out and making specification changes
3 now; if we had known enough about the battery in the beginning
4 we could have generated a specification that encompassed these
5 types of things and here I am in full agreement with the
6 gentleman who made the keynote address, that we should strive
7 not only in the area of silver-zinc but also nickel-cads to
8 come up with a standardized type of specification sheet or
9 standard approach to batteries so that we shouldn't have to go
10 through this sort of an exercise in the midst of a program;
11 we should be able to know as much about the battery when we
12 start with it, rather than having to find out by experience.

13 To recount another occurrence that happened to me
14 several years ago along this same line, we had designed a
15 battery or created a specification for a 2-1/2 ampere-hour
16 battery to be used as a power supply for rain safety and
17 telemetry type systems. A couple of years later a requirement
18 came along where we wanted to blow some squibs, a very high
19 load but of very short duration. There were some people who
20 wanted to take our main missile battery, which was about a
21 30 ampere-hour battery and its specification lent itself
22 somewhat to those loads, and I wanted to take the 2-1/2 ampere-
23 hour battery and make it a pyrotechnic battery.

24 Fortunately I had a lab at the time and had some
25 test specimens around and was able to prove I could do it, but

1 otherwise I am afraid I would have lost the battle there.
2 It was essentially taking advantage of an inherent characteristic
3 of the battery. And on the same battery I have come full cycle
4 again now; I want to use it for another application where the
5 rate is higher than what the specification says but it is an
6 inherent characteristic of the battery.

7 That sort of closes up my remarks on batteries.
8 I would like to reiterate though, again, it would be nice to
9 have a spec sheet on batteries that looked like a transistor
10 spec sheet. It makes it much easier for us to describe to
11 the vendor what we need, and of course he cannot generate all
12 of this information, some of this we have to feed back to him.
13 So there is a need for communication back and forth.

14 Thank you.

15 (Applause.)

16 BILLERBECK: Do we have any questions.

17 Dr. Fleischer?

18 FLEISCHER: Did you keep track of the voltage during
19 stand after activation?

20 MIKKELSON: Yes, we do.

21 FLEISCHER: What was the shape of that curve?

22 MIKKELSON: With reference to --

23 FLEISCHER: Did it stay at a steady value? Was it
24 1.8? Was it lower?

25 MIKKELSON: Oh, are you speaking of the storage

1 effect problem that I had now?

2 FLEISCHER: Yes.

3 MIKKELSON: Okay, yes, when you initially activate
4 the silver-zinc type that we have, the open circuit potential
5 is 1.86 per cell, so you come out with an open circuit
6 voltage of about 35 volts; so open circuit-wise when you look
7 at the battery initially, it looked all right. It wasn't until
8 we loaded the battery that the voltage was lower than what we
9 had expected.

10 Subsequently we recharged the battery and pre-loaded
11 it and then discharged it and found that actually our steady
12 state voltage was about half a volt higher than -- in, fact,
13 it was like a new battery.

14 FLEISCHER: And these are primary batteries?

15 MIKKELSON: Yes, these are primary.

16 FLEISCHER: Cellulose separators?

17 MIKKELSON: I believe that they are cellulose
18 Viscon or visking type separators that are utilized, that is
19 correct.

20 FLEISCHER: On aging of many of these batteries,
21 even if you have Ag_2O , the silver-oxide at the monovalent
22 level you are liable to form silver carbonate and this is
23 especially true of cells even in the dry state which have AgO
24 and once you form silver-carbonate and you activate you have
25 a reaction going on in which silver-carbonate on the surface

1 is reacting slowly and being converted back to silver-oxide
2 and the carbonate going into solution; so that if this happens
3 this may explain why your voltage is not up to par during the
4 period.

5 Silver-carbonate is very easily detected; if you open
6 up the plates of cells and look at the plates, you will see
7 yellow crust. This is a dead sure sign that you have got silver-
8 carbonate. It sounds from what you said that you have a
9 silver-carbonate formation probably.

10 MIKKELSON: I think that is probably true because
11 storage-wise there was no attempt to control the storage
12 temperature of the battery and it is not a sealed battery in
13 the sense of the word, so that is probably what has occurred
14 here.

15 On a recharge cycle, what happens to the silver-
16 carbonate? Is it still present in the battery?

17 FLEISCHER: If it is a rechargeable battery, then
18 the silver carbonate actually doesn't take part in recharging.
19 It stays in solution. You are just losing some of the hydroxide
20 iron present as carbonate. If you get enough of it then your
21 efficiency of charging will go down.

22 MIKKELSON: We noticed that our voltage was higher
23 on the subsequent discharge. Would that be what you would
24 expect, then? When we subsequently discharged we noticed that
25 the voltage was higher. In fact, like a new battery.

1 FLEISCHER: Well, that is because you have converted
2 the silver to the higher oxidation state and you have more of
3 it present in the higher oxidation state. Silver-carbonate is
4 in the monovalent state. It only forms after you form Ag_2O .

5 MIKKELSON: I see, okay. Thank you.

6 BILLERBECK: Any other questions?

7 All right. Thank you very much.

8 Incidentally, I have heard the remark several times
9 recently that it certainly would be nice if we had a
10 specification for batteries that was like a transistor spec.
11 I certainly agree. But I think we recognize that we have a lot
12 more parameters to deal with than one typically has in a
13 transistor and I think their effects are much more subtle, as
14 a number of us are aware in trying to come up with some sort
15 of specification for the nickel-cad cell.

16 And I am sure some of the efforts here at Goddard
17 in attempting to do the same thing with silver-zinc are
18 running into some of the same problems certainly.

19 So, I am afraid it is not as easy as we would like
20 it to be nor as the systems people would like it to be in the
21 spacecraft.

x 22 Our next speaker is William Nagle from Lewis Labs,
23 NASA-Lewis, and he is going to talk about heat sterilizable
24 silver-zinc cells.

al Reporters, Inc.

25 NAGLE: Sometime back in history we decided -- I

1 think Ernst decided -- we should have a fuel cell membrane
2 that was inorganic so that we could raise the temperature on
3 the dual membrane fuel cell. We had this program going with
4 Astropower Laboratory. He said that the dual-membrane fuel
5 cell wasn't going to be a success, so we should put it into
6 silver-zinc cells.

7 This began to look better when we dealt with the
8 5 ampere-hour silver-zinc cell but we were building rigid
9 cookies as separators. If you dropped these things any higher
10 than your chin, and Ivan Blake knew exactly how to drop them
11 from chin high and make them stay alive -- anybody else would
12 break them to smithereens. But these hard cookies for the
13 5 ampere-hour inorganic separator were very hard to put into
14 batteries, too.

15 During the last approximately two years we have
16 a semi-flexible inorganic separator for silver-zinc batteries.
17 Because of a contracting officer requirement that says we will
18 not have quarterly reports any more, none of you have heard of
19 these silver-zinc batteries with inorganic separators. Those
20 that get the monthly reports have heard.

21 All that we have been getting are monthly reports
22 which has the very limited distribution.

23 The thing that I want to do today, since Astropower
24 is going out of business as far as batteries are concerned,
25 and I believe this to be a fairly successful development, is to

1 just give you some of the data that we have assembled in the
2 last two years on the 40 ampere-hour inorganic separator
3 silver-zinc cell.

4 (Slide.)

5 It looks like it is a little wide. In the first
6 line across there is a design that we put together when the
7 first requirement for a Viking program came out. We froze the
8 design so far as the inorganic separator construction was
9 concerned, and said this should be the one that we can sterilize
10 for 200 hours at 135 degrees C. and get some reasonable stand
11 and cycle life out of it.

12 As you can see, this is a small cell, three plates,
13 only 7 ampere-hours. We let it stand charged for 8 months.
14 The voltage remained 1.86. Since that time we have been cycling
15 on a 24 hour cycle, two hours' discharge to 20 percent depth,
16 approximately, and the total wet life of the cell is 24 months
17 so far. It is still cycling.

18 These cells, again, have gone through 135 degrees C.
19 for 200 hours at the beginning of life.

20 The preliminary design that we had for the cell was
21 32 ampere-hour. We have two cells that we let stand seven
22 months and the VK-1 regime relates to the Viking '73 launch
23 which is at 20 percent depth over a 22-hour discharge, 22-hour
24 charge. We didn't hit the day quite right but since its
25 birthday is fairly close we used that.

1 After their charged stand on this preliminary design
2 again you see 269 cycles on the 20 percent depth in 24 hour
3 regime, and the total wet life of these cells, again, after the
4 sterilization period, is so far 18 months.

5 Cells that were float-charged seven months and then
6 cycled on the Viking '73 regime, again there are 269 cycles.
7 These data are 30 days old so that is probably 299 at the
8 present time and 19 months.

9 Here is our only failure so far on this cell
10 construction. Some cells which we had run through our current
11 density temperature cycling regime to find out what kind of
12 currents we could draw on this separator, we had two cells --
13 one cell failed at 463 cycles and one cell at 1,093 cycles.

14 These failures were from silver penetration through
15 the edge of the separator where we had them glued together
16 an enveloped. The present design, are actually what we call
17 the 40-7, 45 ampere-hours actual, nominal 40 ampere-hour.
18 So far these 15 cells are on 50, 75 and 90 degree wet stand
19 and the ones at 90 degrees are just beginning to come off the
20 peroxide level.

21 Several cells have dropped down to the 1.60 voltage
22 but we think they will be all right when the end of the storage
23 period comes -- I believe it is going to be 21 months.

24 Then we will start cycling on the VK-2 regime which
25 consists of two cycles a day, one at 10 percent and one at 20

srs 38

1 percent and this is the one that was scheduled for the Viking
2 75 launch.

3 We see the cells on charge stand, the cells at 90
4 degrees have started to fall off the higher voltage level.
5 Of course, the ones on the float charge, 5 cells each at 50,
6 75 and 90 degrees are 14 months old and still alive.

7 Over here at this side, these are cells which have
8 gone through, again, probably the current density temperature
9 cycling to see what kind of currents we could stand on the
10 cells.

11 We have a range on these 16 cells all grouped under
12 one heading, 330 cycles, on, again, the 20 percent depth and
13 an average of 13 months on those cells; and using the two cycles
14 a day, 20 and 10 percent depth, we have eight months' life,
15 300 to 348 cycles. Then this VK-3, since we were calling all
16 tests VKs of some sort, is a three cycle a day 40 percent depth.

17 Those are two month old with only 70 cycles on
18 them.

19 Again, let me say that all of these cells have been
20 through something that silver-zinc cells cannot stand, 135
21 degrees for 200 hours.

22 This work was done at Astropower by Al Himy who,
23 of course, -- Astropower is going out of business. We will get
24 a report out on this and give it the widest distribution
25 possible. If you are not on our distribution list, and would

1 like a copy of the report, let me know and I will put you on
2 the distribution list for it.

3 The thing that we hope to do at Lewis with this
4 inorganic separator is to bring it in house. We believe that
5 it will improve the life and the cycle characteristics of the
6 silver-zinc cell and we think it will improve it much more
7 if we don't give it that 135 degrees at 200 hours.

8 Are there questions?

9 (Applause.)

10 BILLERBECK: Ernst Cohn from NASA?

11 COHN: (NASA) I would like to make a comment on this.
12 I squeezed Nagle before and asked him just exactly what real
13 power density he is getting out of these.

14 He tells me at the 20 percent level it amounts to
15 about 9 watt hours per pound. So, at the 40 percent level it
16 would be somewhere around 18 watt hours per pound which looks
17 like a pretty promising development if the life can stand up.

18 As he said, you don't necessarily have to heat it
19 for 200 hours at 135 degrees heat.

20 BILLERBECK: I certainly agree, Ernst; that is a
21 very interesting performance.

22 I guess the other question that comes to mind is
23 whether there is going to be any continuation of that work in
24 the future. Would you like to comment on that or would you
25 Prefer not to at this time?

1 COHN: (NASA) He just said he hopes to do it in
2 house..

3 BILLERBECK. I see.

4 Incidentally, we are going to have one more paper
5 and then take a coffee break this afternoon,

6 The next speaker is Mr. Hennigan, and he is going to
7 talk about automatically activated silver-zinc cells.

8 HENNIGAN: (NASA) This also includes some of the work
9 that was done on the converters.

10 Just a block diagram of it. One of the things I
11 think everybody would like to have -- a kind of ideal way to
12 run a battery is to run one cell in the battery without all
13 these series cells that we have.

14 A couple of years ago we had a project that we were
15 were supposed to get at Goddard but unfortunately it went away,
16 but to have a battery that would last from about three to five
17 years and then the only use of it would be when we approach
18 to plan it and orbit it for about six months.

19 The orbiting time would be something on the order
20 of 12 hours to 24 hours; nobody was really sure about the
21 orbiting time.

22 We had developed a converter in house here to work
23 from about 1 volt to 2 volts, to put out at 50 to 100 watts
24 at about 75 percent efficiency. Of course, we could use the
25 ni-cad or silver-zinc with this. Of course, a three to five

1 year life storage isn't usually attainable with silver-zinc
2 batteries.

3 (Slide.)

4 We developed a cell, one single cell that we could
5 fill when we needed it. It has an explosive device in it too
6 fire at a knife and then we release a spring to push a
7 collapsible diaphragm to put the electrolyte in the cell.

8 Now, as you know, when you work with silver-zinc
9 cells this way and fill them you always get gasing. There are
10 two approaches we use: either the cell should be dry charged
11 or we would form it at a very low rate.

12 There was no requirement to fill the cell fast. We
13 didn't care if it took a matter of minutes; it was not a fast
14 requirement. We would have plenty of time to form it if this
15 was the way we wanted to go.

16 The little gadgets on the side are diffusion
17 membranes which will diffuse the hydrogen and oxygen to a
18 lesser degree; hydrogen is the main gas we are concerned with
19 here. In this particular one we were going to put it back in
20 the tank that we took the electrolyte out of.

21 In some cases the experimenters do not want any
22 out-gasing or gas around the satellite; but it was never really
23 decided whether we should do this but you could just let it
24 diffuse to the vacuum in space.

25 (Slide.)

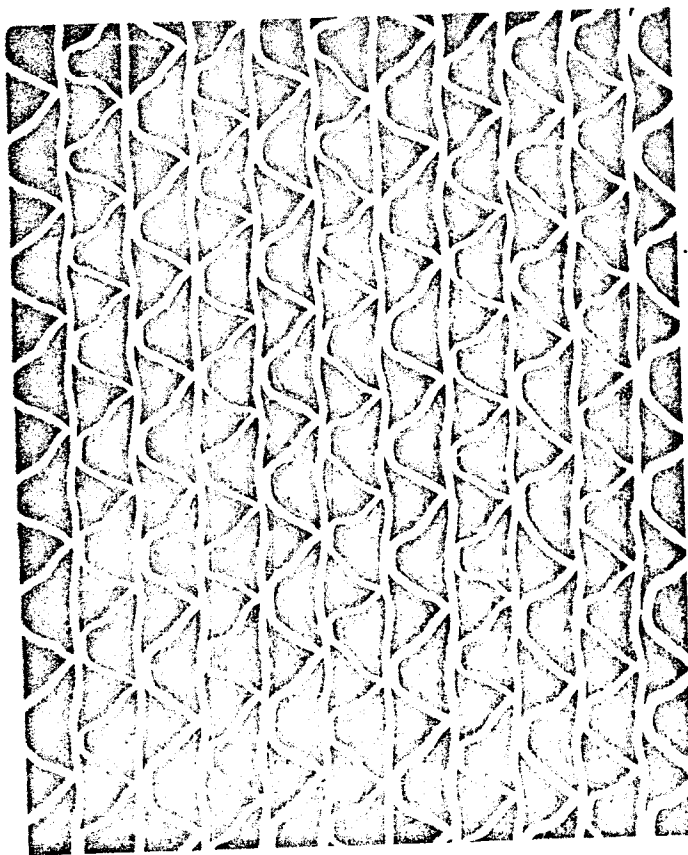
WJ NAGLE
JULY 1968 ZINC WITH MERCAPTAN SEPARATORS

TABLE IV
STATUS OF TEST DATA OF ALL CELLS OF DESIGN TYPE b/b'

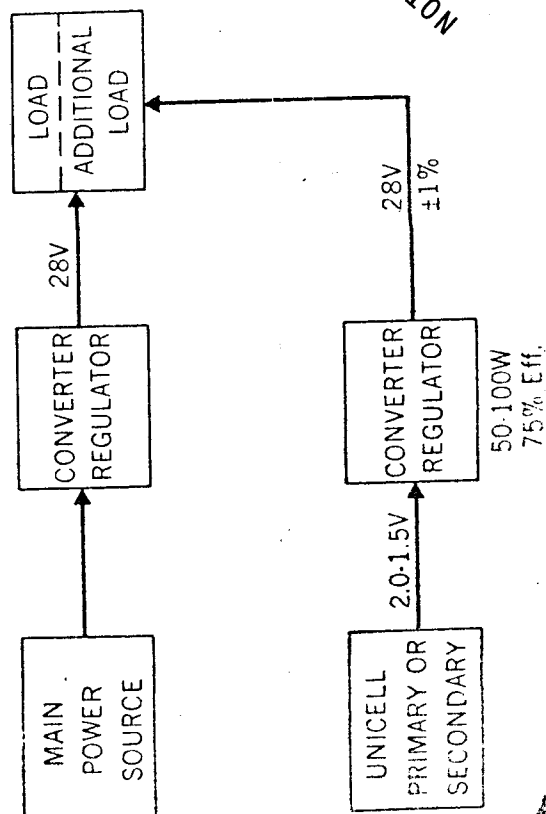
| Group | Original Capacity | Cells | Wet Stand Followed by Cycling | | | | Cycling | | | |
|--------------------------|-------------------|-------|-------------------------------|---------------------|------------------|---------------------|--------------|---------------|---|--|
| | | | Charged Stand | Regime/Stand Cycles | Total No. Cycles | Float Charge Cycles | No. of Cells | Regime Cycles | Total Wet Life | Wet Life |
| 3-Plate Cells (40% KOH) | 7 Ah | 4 | 8 mo. (VK-1) | 428 | 24 mo. | -- | -- | -- | -- | -- |
| Preliminary | 32 Ah | 2 | 7 mo. (VK-1) | 269 | 18 mo. | 2 | 7 mo. (VK-1) | 18 mo. | 2 | 40% Depth (Failed) 5 cy/day 1 cell = 1095 (Failed) |
| Present Design (45% KOH) | 45 Ah | 15 | 14 mo. | -- | 15 mo. | 15 | 14 mo. | 15 mo. | 16 (VK-1) 330-381 13 mo. 4 (VK-2) 302-348 8 mo. 5 (VK-3) 70 2 mo. | |

VK-1 = 1 cycle/day
VK-2 = 2 cycles/day
VK-3 = 3 cycles/day

DAC-60989-M2



APPLICATION OF THE UNICELL



NOT REPRODUCIBLE

1 This is what they had in mind at the time. Of
2 course, we have a main power source, RTG or solar array with the
3 conventional converter regulator and we would be supplying some
4 load during the flight.

5 As we approach the planet or orbit the planet they
6 want the additional loads so this is when the cell will be
7 turned on as a primary or a secondary; of course, we are going
8 to shoot for the secondary. The voltage can actually go as low
9 as 1 volt but the efficiency will go down to about 70 percent
10 if we go that way. And the regulation on the outputter
11 converter is 28 volts plus or minus 1 percent.

12 The tank plus the 300 ampere-hour cell gave us about
13 30 watt hours per pound if it was all foamed in together but we
14 could do about 35 watt hours per pound if we just packaged the
15 tank and the cell separately in here.

16 We really didn't think we had to foam this whole
17 thing in together.

18 One of the things is, I am a little bit concerned
19 about vibrating a cell of this type when it is dry. About a
20 year ago I had a cell vibrating with test electrodes.
21 According to the delta launch vibration schedule, which isn't
22 too bad a vibration, to tell you the truth -- nothing like the
23 military does -- and surprisingly enough, the Teflonated
24 electrodes held up fairly well. If we do any more development
25 on this we would have to have some way of holding that stack, I

1 am pretty sure.

2 We just built a couple of prototypes and since the
3 project is kind of -- we can't find it or it has gone away
4 some place -- we don't intend to do anymore development of
5 this thing but I think the main thing is I would want to let
6 you people know there is such a converter-regulator available
7 for single cell operation at fairly good efficiencies.

8 Thank you.

9 (Applause.)

10 BILLERBECK: Do we have some question now on Tom's
11 paper?

12 SULKES: (U.S. Army Electronics Command) Do you
13 have any idea of the cost of that regulator or what it could
14 be made for?

15 HENNIGAN: These have been built in house and it is
16 kind of hard to get your cost. They did fly one on Nimbus.
17 That one was working at 3 volts. I will make a quick guess.
18 I would say something like \$10,000 to make one or two.

19 BILLERBECK: Other questions?

20 GROSS: (Boeing) Just a minor point. I wondered
21 about this concept of separating hydrogen by diffusion and I
22 calculated it one time and I doubt now whether it operates
23 according to the square root of the electrode weight or the
24 electrode itself, but in either case it turns out that you still
25 diffuse out too much oxygen. You have to worry about oxygen

1 diffusion also as well as hydrogen.

2 HENNIGAN: Well, we have done silver-zinc cells
3 without overcharging at all and involved no oxygen during
4 the charge cycle.

5 GROSS: Okay, you had low enough oxygen; you didn't
6 have to worry about it.

7 HENNIGAN: What we would use is this technique where
8 we sense the current and when it tapers down we drop the charge
9 to just above the open circuit, about 187; and we have run
10 cells on for at least a year with very little pressure buildup;
11 maybe 2 atmospheres at the most over the whole time. And most
12 of that is hydrogen, so we would lose a little bit of oxygen
13 but I don't think that would bother us over say six months'
14 time.

15 Now, we have used this diffusion method in a sealed
16 satellite where we had -- silver zinc cells, fairly large
17 size up to 200 ampere-hours size, and we had to be careful
18 that we didn't get water vapor into the satellite that would
19 affect the electronic instruments. So over each one we had a
20 little diffusion membrane and did diffuse out oxygen. There
21 was another time that we did use charging these cells again
22 at very low rate.

23 I think over six months we might have cycled --
24 what was it Charlie, about ten times? About ten times or so.

25 BILLERBECK: Other questions on this paper?

1 All right, I think now Ernst Cohn would like to make
2 a comment here at this point on another matter.

3 COHN: NASA) This is a bit on the impromptu side,
4 but since it said new developments for this afternoon I thought
5 I would mention it to you quickly that we are trying to
6 develop something newly that was started about -- I don't know
7 whether it was 15 or 25 years ago by Dr. White and his crew
8 at NRL -- that is a non-gassing ni-cad cell. It should be
9 possible, according to him, to build non-gassing ni-cads in
10 which you are negative limited, where you replace the nickel
11 screen with something that gives you a higher hydrogen over-
12 voltage so that you can then use a voltage setting if you have
13 a proper type of material, use a voltage control to cut off
14 the charge when the negative is fully charged, have enough
15 excess positive so that you don't develop any oxygen and
16 thereby in principle you should be able to build a non-gassing
17 ni-cad.

18 The advantages would be manifold that I can see.
19 I haven't heard of any great disadvantage yet. I don't know
20 why nobody has really pursued the matter, but we are now going
21 to try in a very modest way to go about this.

22 I talked to a number of people, including some of
23 the people here, about it, but I thought I would use the forum
24 to mention it again and to mention also that Mr. Uchiyama of
25 JPL, who is sitting back there, is going to handle the program

1 on very modest means.

2 Thank you.

3 BILLERBECK: Thank you,

4 Now, Gerry, did you have any comments before we take
5 our coffee break here?

6 HALPERT: (NASA) Yes, I would like to have slides
7 or Viewgraphs from people who have not turned them in to me
8 so we can have them photographed for the proceedings.

9 BILLERBECK: Fine. I think that is very important
10 and it certainly will contribute to the quality of the papers
11 from this meeting if we can get all those slides. I think
12 there were some very good ones.

13 Thank you.

14 (Recess.)

15 HALPERT: To conclude the sessions for
16 today, this last portion will be an open discussion.

17 I would like to ask if there are any subjects or
18 questions that people have that they would like to ask the
19 group as a whole and have people respond to.

20 Are there any areas you feel should be covered
21 additionally or that have not been covered that they would like
22 to mention and get some response to?

23 Bill Nagle?

24 NAGLE: (NASA) I would like a discussion on the
25 causes of fading in the cadmium electrode. I have heard some

1 some discussion of things that don't fade, but I still don't
2 know why we are getting it.

3 HALPERT: Is there anybody who would like to open
4 the discussion on fading? Dr. Fleischer?

5 FLEISCHER: I think as a starter Bill Nagle ought
6 to get up and give us a talk and show the cases where this
7 fading has been authenticated and the conditions under which
8 the cells have operated, charge conditions, discharge conditions,
9 open circuit times, and then we will have a point at which we
10 could start talking about what is is we want to know about
11 fading.

12 NAGLE: (NASA, Lewis Research Center) As far as I
13 am concerned, it is still just a rumor that happened recently.
14 I haven't seen any examples of fading. I want to know where to
15 hit the problem if there is a problem.

16 HALPERT: We have experienced some, to my knowledge;
17 I am not in on any of the satellite projects but I am sure some
18 of our project people here have seen it.

19 I wonder whether we could get a comment from --
20 Steve, would you like to say something?

21 GASTON: (Grumman) I don't have the data with me
22 showing the fading and I wasn't prepared for that, but I am
23 quite sure we can get the information. It is available.

24 I don't think it is a rumor; it is a reality and it
25 does exist. The negative electrode does change in its

1 characteristics either as a function of age or a function of
2 cycling and doesn't accept the charge anymore as it did before.

3 I think a study was made under Goddard's sponsorship
4 looking at the crystalline structure of the cadmium-hydroxide
5 crystalline, that crystals certainly did change from a very
6 regular crystal to a very irregular, very thin crystal. I
7 am quite convinced the negative electrode does change its
8 crystalline structure and I am also convinced that because of
9 this change the capacity of the negative electrode does change.

10 HALPERT: Steve, do you care to say what the
11 characteristics are, what do you see that indicates that the
12 negative is fading? What are the particular electrical
13 characteristics you see?

14 GASTON: One thing you definitely see is when you
15 do charge the cell under an orbital regime, you will note that
16 the charge acceptance to a specific voltage you potentially
17 charge -- acceptance is going to be lower, but if you charge
18 to a fixed input that you will see a higher voltage. We have
19 seen instances where, based on the auxiliary electrode signal,
20 that we do have a voltage rise but no corresponding rise in
21 the auxiliary electrode signal, showing that the cell is
22 negative limiting. I should say indicating that the cell is
23 negative limiting.

1 temperature overcharge which I showed yesterday, I see an
2 indication of change in the charge characteristic -- the over-
3 charge characteristics.

4 HALPERT: Just to clarify this, you say you see a
5 higher voltage at the end of charge, is that what you are
6 saying?

7 GASTON: On the overcharge characteristics, yes.

8 HALPERT: This is a separate test, overcharge
9 characteristic?

10 GASTON: Separate from the normal characteristic; in
11 the normal charge characteristics you will see a rise in cell
12 voltage with no corresponding rise in the -- signal voltage,
13 and that is pretty much indicative or apparent that it is
14 negative limiting.

15 WILL: (G.E.) I would like to continue my pitch
16 of yesterday. Apparently Dr. Nagle might not have been here
17 yesterday.

18 There was also, of course, one of the leading talks
19 yesterday by Dr. Beauchamp from Bell Telephone that showed very
20 nicely the performance which he called of a commercial plate
21 that undoubtedly showed the effects of loss of capacity on
22 cycling and he compared that very nicely with the plates which
23 they have produced recently using the electrochemical impregna-
24 tion process.

25 So I think we are, number one, dealing with a true

effect and, number two, I would like to discuss maybe some of the aspects of fading.

We have recently, under NASA contract sponsorship from NASA Research Center in Cleveland, performed a study which I mentioned yesterday very briefly in which we have identified two major reasons for the loss of capacity on continuous cycling.

Number one, there is undoubtedly a very large increase of particle size which we find to exist especially at the larger temperatures. In fact, under the microscope we observe the first particle growth to occur in the very first discharge.

At room temperature, in the microscope, under magnification of 500X, we did not observe such particle growth in the first roughly ten to 20 cycles. However, if one increases the resolution of this study by taking the plates to the scanning electron microscope, one does observe particle growth which also starts as early as in the very first discharge.

Now once these big particles have been formed, they are very difficult to cycle; they are just too large. They are cadmium-hydroxide crystals. We have identified them as such; they are very large in size. And it is sort of obvious that with the slow ionic processes taking place in these large crystals of cadmium-hydroxide, that it is very difficult to

1 reduce them all the way through to cadmium.

2 We have observed these big particles to just sit
3 there in the electrode, maintain their size; if anything, they
4 grow on cycling more and more; they don't participate in the
5 cycling; they don't, therefore, contribute to the capacity.

6 We have also identified a second reason for the
7 fading and what I am hinting, therefore, is that there is no
8 simple answer to this complex question.

9 We are not dealing with one simple phenomenon; we
10 are rather dealing with many different phenomena superimposed.
11 It will depend on the particular cycling regime one uses,
12 things very pertinent which Dr. Fleischer brought up a moment
13 ago. It depends on how long one keeps the electrode on open
14 circuit, what the cycling regime is, whether one overcharges or
15 overdischarges. All of these factors play a significant role
16 as to what fading mechanism might exist.

17 Now to the second point I wanted to make. The
18 second reason for the failure we identified is the formation of
19 passive films. These films show a brown color. One should not
20 confuse that with cadmium-oxide, however, because we have found
21 these brown films to resist reduction. While, on the other
22 hand it is very well known that cadmium-oxide, the brown
23 cadmium-oxide, can readily be reduced to cadmium.

24 It is most likely that these brown films consist of
25 cadmium-hydroxide which contains a high concentration of defects

1 which act as color centers and produce the brown color. It
2 is these defect-rich hydroxides which are passive, because
3 most likely their ionic conductivity is low.

4 As I also said in my pitch yesterday, some of these
5 things I have said now will be published in a NASA report
6 forthcoming in the next few months.

7 HALPERT: Jim Dunlop, COMSAT.

8 DUNLOP: (COMSAT) I also think we are covering this
9 subject pretty thoroughly but I would like to add that
10 yesterday morning I presented a paper describing results on
11 the IntelSat-4 Program where we made an attempt to analyze
12 cells at different stages in a test program, from the time that
13 we received the cell from the cell manufacturer up to one year
14 later in the test program.

15 Let me give you the results that we have, briefly,
16 and then I want to make some comments with respect to what was
17 just said.

18 Before, as we received the tests, that is before
19 we did any cycling, we were able to obtain about 80 percent
20 utilization of the cadmium electrode. After we ran 30 cycles
21 of burn in, we took three cells, we got 72 percent utilization
22 on one and 73.5 on another and 74 percent on the third one.

23 That was the utilization after 30 cycles with an
24 80 percent depth of discharge, charging back at a C over 10
25 rate, discharging at a C over 2 rate, charging it for 16 hours,

1 discharging it for 1.2 hours.

2 We then put this cell into a real fine test program
3 where we ran it through an eclipse operation with a varied
4 depth of discharge each day, a varied profile each day, and
5 then went into a storage mode. After one year of testing, we
6 took two cells out and one cell had 70 percent utilization,
7 the other had 70.5.

8 So there was a gradual decrease in the utilization
9 of the negative electrode as a function of time.

10 The second point here is, the utilization of this
11 material was interesting in what part of it we were utilizing,
12 where we limited it on charge or where we limited it on
13 discharge. Initially, when we first received these cells,
14 when we completely discharged the cell electrically, electro-
15 chemically, we completely discharged it at a useful rate and
16 then go through a chemical analysis because we find there is
17 still metallic cadmium remaining in that plate which cannot be
18 discharged.

19 We also find that when we try and charge this same
20 plate in a flooded condition and then go back and compare it to
21 the chemical theoretical capacity, that we cannot fully charge
22 this cell; this is somewhat in agreement with what was just
23 said, that there is some cadmium hydroxide here which cannot
24 be charged. And it turns out that with cycling it seems that
25 the amount of cadmium hydroxide that cannot be charged is what

1 is increasing or causing the loss in utilization, that the
2 amount of metallic cadmium remaining in the plate is actually
3 diminishing with time.

4 HALPERT: Dr. Weininger?

5 WEININGER: (G.E.) I don't think anybody defined
6 fading with a simple sentence. I want to ask whether I am
7 right in saying that fading is the irreversible loss of
8 negative capacity. Am I right or am I wrong?

9 If I assume to be right, then I will continue
10 because if you --

11 VOICE: Not really.

12 WEININGER: Okay. If I am wrong I want you to tell
13 me, please.

14 HALPERT: Does anyone want to answer that?

15 DUNLOP: (COMSAT) The point I just made is that at
16 the beginning of the cycling there was metallic cadmium in that
17 plate that we could not discharge initially that with cycling
18 we were able to discharge.

19 HALPERT: Dr. Fleischer.

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4 FLEISCHER: I ran discharge tests on negative plates
5 in a fully flooded condition under many conditions of charge
6 and discharge. For example, on the regime of low rate charging,
7 say 20 hour charging, with 100 percent overcharge, and the
8 rate at which you lose capacity is a function of discharge
9 rate and usually on sintered plates there was an intermediate
10 rate at which it was the maximum.

11 And this depends on the thickness of the plate. On
12 80 mill plates it happened at the maximum loss of capacity was
13 at the one-hour rate which was higher than at a 5-hour rate
14 or at a 10-minute rate.

15 If you carry those plates down to the point where you
16 only have 20 percent of their original capacity, you could
17 bring the capacity back by giving them a higher rate charge, in-
18 stead of charging them at overnight, say 15 hours, with 100
19 or 200 percent excess over capacity, you charge them in three
20 hours at the same input, now you would find that the capacity
21 started to come back up. So I cannot agree that it is
22 irreversible in the sense that you cannot get it back somehow;
23 but in a battery you would have great difficulty in carrying
24 out this reconditioning to get to the same condition.

25 WEININGER: That really answers most of my point,

1 namely, that I was particularly interested in the irreversible
2 aspect. It it is reversible or if it changes as Fritz said
3 by a change in crystal size or as Dick Beauchamp yesterday
4 discussed as a possible mechanism of closing pore size. This
5 is just a redistribution of cadmium.

6 What I was really trying to allude to was that we
7 have in the literature back five or ten years lots of examples
8 where people have found just exactly that redistribution and
9 if you have any particular changes due to C rate, well, that
10 is a different story and I will agree that the mechanism of
11 that hasn't been fully explored.

12 But just the decay of capacity, that can very
13 simply be explained by the redistribution of the the material.

14 Thank you.

15 WILL: (G.E.) Since I have this in my hand anyway --

16 (Laughter.)

17 WILL: -- I completely agree with Dr. Fleischer that
18 one ought to distinguish between irreversible and reversible
19 loss in capacity. In fact, it appears that most of the capacity
20 under proper conditions can be put back into the plate.

21 Now, the redistribution that Dr. Weininger mentioned
22 has been observed quite early. This is quite true. However,
23 the mechanisms leading to these changes have until recently
24 been completely unknown.

1 solubility increases sharply, with increasing KOH concentration
2 and with increasing temperature, and we have recently in this
3 NASA study shown beyond any doubt that cadmium does grow into
4 solution, then can obviously leave the plate and it has been
5 known, of course, that -- it then becomes deposited into the
6 separator and can give a lot of trouble.

7 With regard to the mechanism, the only thing I
8 wanted to add on now is the significance of changes of pH in
9 the battery plate itself; and it is those particular pH
10 gradients with which we have dealt a lot at G.E. in the past
11 few years.

12 There is something very peculiar about it in that
13 on discharge, of course, we are consuming hydroxyl ions in the
14 plate and we also know that at lower pH cadmate is less
15 soluble, so we are bound to precipitate, we are bound to over-
16 saturate and precipitate; and the large crystals which I
17 mentioned to be formed in the very first discharge are in fact
18 formed as a consequence of the formation of low pH in the
19 plate and consequent precipitation due to supersaturation, and
20 precipitation of cadmium-hydroxide crystals.

21 On prolonged charging one does just the opposite;
22 one raises the pH, the $\text{Cd}(\text{OH})_2$ crystals can redissolve as
23 cadmate ions and we have shown in several experiments that
24 we are then dealing with an electrodeposition, simply $\text{Cd}(\text{OH})_3^-$
25 is being discharged to get metallic cadmium and that is

1 the mechanism which makes additional capacity on prolonged
2 charging available again.

3 Summing it up, this last point, on prolonged
4 charging one is producing higher pH, that favors the dissolution
5 of cadmium hydroxide crystals -- that is a slow process -- and
6 if one does it long enough then one can electrodeposit
7 cathodically the cadmium ions back to cadmium.

8 HALPERT: Dr. Fleischer?

9 FLEISCHER: (Consultant) I would like to add some
10 more points to our discussion about this subject.

11 We will go over to pocket-type plates for a minute,
12 and here the active material is a mixture of cadmium-oxide and
13 iron-oxide, iron-oxides in various forms. One of the favorite
14 ones to use is a composition of magnetite having some water
15 crystallization.

16 If you look at the pocket-type plate without any
17 iron-oxide addition you will find within one or two cycles of
18 forming the material the cadmium has agglomerated into a kind
19 of sponge which has practically no discharge capacity -- you
20 just don't seem to have a way of getting a discharge going out
21 of it -- but the minute you add iron-oxide you have changed
22 the whole mechanism of whatever is going on. No one has really
23 explained what happens by adding iron-oxide to cadmium.

24 It is also true that no matter what battery system
25 you look at, you have to have what we call an expander.

1 Probably half of the problems with lead acid batteries
2 are due to the fact that your expander has lost its initial
3 stage of distribution or you have used the wrong one or you have
4 done something with the expander that isn't right. But you use
5 it in practically every case. The only one I don't know of --
6 well, Dr. Lander at Wright-Patterson has introduced Emulpho-
7 gene as an expander for the zinc electrode but their problems
8 have to do with the soluble nature of the zinc.

9 But here everybody is building, as far as I know,
10 cadmium electrodes without expanders and we have this whole
11 background of experience saying, well, you had better get an
12 expander of some kind in here or the cadmium will agglomerate.

13 In this particular case I wanted to bring out that
14 the problem is not in the cadmium-hydroxide but actually in
15 the state of agglomeration of the metallic cadmium.

16 So I will just add that the expanders that work
17 exceedingly well for cadmium are cellulose derivatives which
18 are most unlikely candidates in most cases because eventually
19 they are oxidized to carbonate.

20 I might also say that oxidized cellulose is
21 manufactured by Tennessee Eastman Kodak by oxidizing cellulose
22 with N_2O_4 produces a compound which will bring back almost any
23 cadmium plate. If you add it to the electrolyte and cycle it
24 you will bring back the capacity in a very few cycles.

25 The other expander is indium, the addition of a

1 small amount of indium to cadmium, indium being only slightly
2 soluble in cadmium metal, will act as an expander and probably
3 a very practical one because it increases the low temperature
4 performance of the cadmium electrode. However, the amount of
5 work that has been done on indium addition to cadmium electrodes
6 is very small.

7 We don't know what it will do in a restricted
8 electrolyte cell; we don't know what it will do in various
9 temperatures; we actually know very little of the mechanism of
10 its behavior.

11 CARR: (Eagle Picher) Not everybody doesn't use
12 expanders in the negative, Dr. Fleischer. In nickel cadmium.

13 I would like to go back to some of the discussion,
14 or to go on with a little bit of the discussion. As I under-
15 stood what was said, we can form large inactive crystals of
16 cadmium-hydroxide and we at Eagle-Picher found this also in the
17 work on the failed cells that had been subjected to many, many
18 cycles.

19 The cycle data which I presented those cells had
20 large inactive crystals which we identified as cadmium-hydroxide
21 with a trace of cadmium-carbonate.

22 I cannot quite understand, since there are substantial
23 quantities of carbonate present in the electrolyte in these
24 cells, or there was, that there was not more cadmium carbonate.
25 I don't know if that comes into play with the brown layer that

1 you were talking about or not.

2 I would like to ask a couple of questions. First
3 of all, can you detect any redistribution of negative material;
4 can you tell if it is moving from the inside of the plate to
5 the outside areas, which is what we would suspect. And then
6 further on this, I infer that if you have this and we go to a
7 long-term low-rate charge, we can get it back. I would like to
8 know if anyone has done any failure work on the phenomena which
9 we have discussed yesterday mostly on long-term trickle charging
10 makes capacity less available and seems to be irreversible.

11 WEININGER: (G.E.) I can answer only a very small
12 part of your question but I am awfully happy you asked that one.

13 I will try to be very modest about this thing but
14 these pink booklets there that Gerry Halpert has assembled
15 shows one particular reference about five or six years ago
16 when Eric Lifshin and I took one of the very first Crane
17 series of tests, in Dayton, and have taken these plates, the
18 same material, and done electron scanning, X-ray scanning, of
19 the plates and showed how through a number of cycles, the
20 temperature and depth of discharge the cadmium was moving from
21 the inside to the outside.

22 There were also other methods involved, X-ray
23 transmission and the metallographic as well, so as far as the
24 cadmium is concerned, it moves from inside to outside.

25 Thank you.

GROSS: (Boeing) I wanted to ask Fritz Will a question about the effects of pH changes on the movement, migration of cadmium due to solubility. First, I wanted to point out what is already well known, that the solubility of the cadmium species in addition to being dependent upon pH and temperature is also very highly dependent on concentration of carbonates; so it is quite obvious when you look at the solubility chart of this that you want to minimize carbonate in order to minimize solubility.

One question that comes to my mind is the effects of temperature cycling on the dissolution-precipitation sequence. You would expect a larger temperatures on discharge than on charge, and I am curious what he has found that this might do to the precipitation mechanism.

The other question I wanted to ask was on the use of cellulose. I understand that most manufacturers do use cellulose in their negatives. I don't know if it is justified or not but my question is to the manufacturers: Do they use cellulose in their products? I would like to hear from them.

CARR: (Eagle Picher) No.

HALPERT: Any comments.

RAMPELL: (G.E.) No.

VOICE: Gulton Industries, No.

HALPERT: Gulton Industries says no.

I might make the comment here that that one point

1 that Dr. Fleischer mentioned ironoxide and of the cells that
2 we have seen some of this fading in, I mentioned specifically
3 I am more familiar with the OAO cells which are made with plates
4 that have a nickel-plated steel grid in the center and that
5 nickel-plate not always protects the steel as well as one might
6 expect and there is iron-oxide available and I wonder if that
7 would be the type of iron-oxide that we are talking about,
8 this is my question?

9 WILL: (G.E.) This is in answer to the first
10 question from the gentleman back there -- the brown color in
11 our experiments cannot be associated with the formation of
12 carbonate. We carefully excluded carbonate by suing nitrogen
13 flushing through a polyethylene bag surrounding our micro-
14 scope stage; furthermore, we are dealing with single crystals of
15 cadmium-hydroxide and I don't quite see how carbonate would
16 fit into those single crystals.

17 The brown color was not associated certainly with
18 these big crystals.

19 Temperature cycling on charge and discharge, as far
20 as I understood your question, you are not proposing to control
21 the temperature from the outside but rather you are talking
22 about a temperature change which comes about through the process
23 of charge and discharge.

24 Well, we have not looked into that effect. I would
25 suspect those temperature changes, under the small-current

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1 conditions that we are using in our experiments, that these
2 temperature changes would be very small and I would not think
3 that we are dealing with effects due to these small temperature
4 changes.

5 GROSS: (Boeing) Not in your experiment but what
6 we might expect in experiments with real cells which do show
7 the large temperature variations.

8 WILL: (G.E.) One word on the expanders. As early
9 as 1910, Grube has done a careful study of the effect of Fe_2O_3
10 as well as Fe_3O_4 on the capacity and cycling of cadmium plates
11 and found both of them to be beneficial in preventing the loss
12 of capacity on cycling. He found that the Fe_2O_3 participates
13 in the cycling while the Fe_3O_4 is inert as far as the cycling
14 is concerned and sits there and prevents the fading, probably
15 by acting as nuclei for the soluble cadmate species.

16 So far for the speculation of Grube on the mechanism
17 involved in the facts he found.

18 Later on Otto Wagner, of course, at Fort Monmouth
19 only a few years ago, did a very careful study of the effects
20 of Fe_2O_3 on the fading of cadmium plates.

21 SULKES: (Army Electronics Command) With regard to
22 the study of the iron-oxide, it certainly was very beneficial
23 to the cadmium plate; however, the nickel-cadmium cells
24 lowered the oxygen voltage on the nickel and, in effect, in
25 that type of cell it was not beneficial, whereas it was in a
cadmium

1 air type, so that material alone is not good. There are other
2 materials which may not have that effect and will have the
3 expander properties.

4 I would like to make one comment to Dr. Will. In
5 your studies, this was probably very what we call clean
6 conditions on your cadmium whereas in your normal cell we do
7 have let's call it gunk coming off the separator which does
8 have an expander property and in your pasted cadmium plates
9 and sil-cad, let's call it the gunk that comes from the
10 cellophane does have expanded properties and your fading is
11 not as rapid.

12 HALPERT: Maurer, Bell Labs.

13 MAURER: (Bell) A comment on the temperature
14 effect. Utaka Okinaka presented a paper a few years ago on
15 cadmium electrodes; these were battery electrodes now in which
16 he discharged and charged the electrodes at different tempera-
17 tures and at different rates and looked at them with the optical
18 microscope. And he showed pictures of the cadmium-hydroxide
19 crystals and effects are what one might predict if one would
20 try to grow crystals; low rates and high temperatures on dis-
21 charge, tend to form large cadmium-hydroxide crystals and high
22 rates and low temperatures tend to form small ones. So any
23 type of temperature cycling and rates in this line would tend
24 to form small crystals would be beneficial. In satellite work
25 where you are talking about temperatures of 32 degrees F. and

1 fairly high rate discharges, the tendency would be to form
2 small crystals. This is only part of the picture, however.
3 You still have the long-term trickle charge, for example,
4 where you are talking about charging up some of these crystals
5 and getting the dissolution mechanism to move material about,
6 you still have to provide the other half of the electrochemical
7 reaction because in that state of charge the electrode cannot
8 change while you are on overcharge and that other half turns
9 out to be the oxygen attack on the metallic cadmium that I
10 spoke about yesterday.

11 GROSS: (Boeing) I would like to repeat again,
12 however, that since in real cells the solubility is so temper-
13 ture dependent and since the temperature does cycle in real
14 cells, that this does still remain an open, unanswered question,
15 in my mind at least.

16 STEINHAUER: (Hughes) We talk about expanders and
17 we talk about this fading problem, but what happens when we do
18 everything we can and we still get it?

19 (Laughter.)

20 STEINHAUER: Is the only mechanism getting the
21 higher hydrates of the cadmium back into solution? Second,
22 in commenting on Cohn's paper earlier of the negative limited
23 cell, we may want it to fade, it may become negative limited,
24 but there must be a limit. What about a cell that is positive
25 limited on charge and negative limited on discharge? We would

1 be interested.

2 HALPERT: Any comment there?

3 MAURER: I had a comment on Cohn's comment initially.
4 (A), you can make the hydrogen overvoltage in the cadmium
5 electrode higher by treating it with mercury. This was reported
6 on by Gottlieb a few years ago. That raises the hydrogen over-
7 voltage and give you the effect that you are interested in.

8 We have thought about this type of approach for the
9 Bell System applications; however, in the Bell System we have
10 to be money conscious to provide this type of operation without
11 raising your telephone bill.

12 The problem is in charging a cell of this type in
13 a battery, it is very easy to charge it singly, limit the
14 voltage to 1.6 or 1.5 or wherever you happen to want it. When
15 you put this same thing in the battery, when you put a constant
16 voltage limit on it, there is bound to be a cell with lower
17 capacity that gets charged up first and when it reaches full
18 charge the voltage goes up and if it is a battery with a lot of
19 cells in it, its reaching full charge is not detected in the
20 charging circuit, it voltage will go right on up to the hydrogen
21 evolution potential, whatever that happens to be, so you will
22 get gasing in one cell's battery on charge unless the cells
23 are perfectly matched.

24 The way around this problem is to simply charge the
25 cells in parallel and provide an electronic switching

1 circuitry suitable for changing them from charge mode to dis-
2 charge mode in series. And for aerospace applications I would
3 think this would be practical, especially with integrated
4 circuits.

5 In Bell System service it is rather impractical,
6 I think.

7 DUNLOP: (COMSAT) Was the question answered on
8 what the effect of carbon, the buildup of carbonate is on
9 the positive plate for in general what it is in the cell?

10 I didn't really understand the answer if it was
11 given. If somebody speculated on that. What happens in the
12 buildup of carbonate? What does it do to cell performance?

13 WILL: (G.E.) I would only like to comment on the
14 effects of carbonates on the cadmium plate which has been well
15 documented. The carbonate additions to the COH grossly increase
16 the solubility of cadmate ions in solution and thereby grossly
17 exaggerate the phenomenon of fading as demonstrated by Wagner
18 at Fort Monmouth.

19 DUNLOP: I guess my question really was, with respect
20 to the comment that carbonate, where he said that he would have
21 expected with the amount of carbonate buildup that he had in
22 the electrolyte, that he would have expected to see a larger
23 amount of cardmium carbonate in the cardmium electrode.

24 I think the other question I really would ask would
25 be directed to Dr. Reed, and that is, what was the effect in

1 his test program?

2 GROSS: I would mention that Kroger has recently
3 published a paper indicating some effects of carbonate on the
4 positive; however, it was somewhat qualitative and the
5 conclusions were not quite clear to me, complicated by the
6 fact that they weren't clear enough for me to remember them.

7 I will turn it over to Reed.

8 REED: (Battelle) To answer Dunlop's question about
9 the effects of carbonate on the positive, we have done some
10 short number of experiments in which we cycled some small
11 positive electrodes in KOH in which various amounts of
12 carbonate were added, keeping the potassium ion concentration
13 constant so as to simulate the increase in carbonate
14 formation in sealed cell electrolyte.

15 We found that the charge potential of the positive
16 increases, goes up toward the potentials at which you would
17 expect oxygen to be involved much more rapidly in electrolytes
18 in which there is a high degree of carbonation, say several
19 hundred grams per liter; and when you have pure 30 percent
20 KOH. And likewise the discharge voltage is lower.

21 I say we did just a small amount of work on this.
22 More recently there has been a paper published by General
23 Electric personnel -- I do not recall all of the authors; one
24 of them was Cattoti from Gainesville. This was presented at
25 the Brighton Conference several months ago and there are pre-

1 prints of it available; some people here, I believe, have
2 them. I have seen this paper and they did a similar experiment
3 except they used sealed cells with reference electrodes in
4 them. They found that when the electrolyte had a large degree
5 of carbonate the cell voltage on charge did increase rapidly
6 similar to what we found; in following the electrode, single
7 electrode potential versus the reference electrode in their
8 cells, they found that most of this increase in cell potential
9 was at the positive electrode and likewise the decrease in
10 cell potential on discharge also occurred at the positive
11 electrode.

12 He pointed out, however, that since their cells had
13 a large excess of negative capacity, they could not make any
14 definitive statements about the effect of carbonate at the
15 negative in the short-term cycling that they did.

16 GROSS: (Boeing) That was the paper I was referring
17 to. The specific point that was ambiguous was the fact that
18 carbonate levels investigated in which these conclusions were
19 drawn were extremely high, and would not necessarily be valid
20 in the lower carbonate concentrations we might expect in well
21 made cells.

22 REED: (Battelle) I am not so sure that in the past
23 at least we have not found these high carbonate concentrations
24 in cells. A number of cells that we have had on test at Wright-
25 Patterson when analyzed we found that as much as 50 equivalent

1 percent of the KOH had been converted to carbonate.

2 MAURER: (Bell) I agree with Reed, since in the
3 sealed cell there is very limited quantity of electrolyte;
4 you don't need very much carbonate to achieve a very high
5 percentage in the electrolyte.

6 Physically, in the characteristics of the cell, if
7 you just look at a cell, no reference electrodes or anything,
8 the first evidence of carbonate many times shows up as so-
9 called carbonate step in the discharge plateau. The discharge
10 proceeds in a normal fashion, you get a semi-need and then
11 another lower voltage plateau. Many times this is as low as
12 8/10ths of a volt.

13 There is some question in my mind that carbonate
14 itself causes the higher charge voltage and lower discharge
15 voltage that is observed. Part of this at least can be
16 explained by the lower pH of the electrolyte. You have
17 converted a substantial fraction of the OH ions effectively
18 into CO₃ ions so the pH drops and you get in effect a cell
19 with one normal KOH instead of 7 normal KOH.

20 Another effect was described by, I believe, Turner
21 and Okinaka a while back, a few years back. Carbonate in the
22 electrolyte tends to cause corrosion of the nickel substrate
23 of the positive electrode and so operation with large amounts
24 of overcharge would tend to corrode the positive electrode.

25 The first effect you see is an increasing capacity

1 and eventual drop in capacity because the plate falls apart.

2 HALPERT: You are talking about the carbonate
3 coming in with the electrolyte, not as part of a separate
4 degradation.

5 MAURER: In Turner's work he deliberately added
6 carbonate, but the same thing can happen in a sealed cell where
7 the carbonate comes from the separator degradation.

8 Another effect is the freezing point of carbonate-
9 KOH mixtures is, of course, higher, and so for low temperature
of tape 10 performance presence of carbonate causes problems.

11 FLOYD: A point to be clarified. I think maybe Dr.
5 p.m. 12 Reed can clarify this.

13 When you say that the charge voltage as it increases,
14 it has been my experience that when you talk about charge
15 voltage you have two very distinctive regions to be concerned
16 with. One is the charge voltage prior to going into overcharge.
17 The other is the overcharge voltage itself at whatever
18 constant current you may be charging which is usually at a
19 fairly low rate.

20 Which one or are you talking about both of these
21 voltages increasing?

22 The second point, addressed to Dr. Maurer, did I
23 understand you to say that the double plateau effect that we
24 see on cells, practically all aerospace cells with extended
25 cycling, is due to carbonate?

1 REED: (Battelle) The portion of the charge
2 voltage curve which I am referring to starts out immediately
3 and rises rather than remaining fairly flat with a slow increase
4 in potential until most of the positive is charged and,
5 likewise, the curves at General Electric show almost an
6 immediate increase in charge potential.

7 MAURER: (Bell Labs) Part of this effect is due,
8 also, I forgot to mention, to the fact that carbonate and KOH
9 mixtures have a higher impedance than a set of normal KOH,
10 so you see a higher charge voltage simply because the IR drop
11 in the cells is higher and consequently on discharge a
12 suppression.

13 Whether all of the second plateaus on aerospace
14 cells are a carbonate effect or not, I wouldn't care to
15 mention since I haven't looked at them personally. It is very
16 likely that that could be part of the problem.

17 There are other effects that can cause voltage
18 (changes).

19 REED: (Battelle) Regarding the increase electrolyte
20 resistance in KOH-carbonate mixtures, the increase in cell and
21 single electrode potential is much greater than one could account
22 for simply on the basis of IR loss; furthermore, if it were
23 simply that it should not show up when you do measure it against
24 the reference electrode and the increase in single electrode
25 potential versus the reference electrode is almost identical to

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1 that of the increase of cell voltage when the electrolyte has
2 a high carbonate concentration.

3 HALPERT: It has been decided a long time ago that
4 carbonate is not very good for the cell, at least it causes
5 problems and depending upon how much carbonate in there you
6 want to increase your pre-charge, if I may say that word at
7 this time, to that much greater extent.

8 DUNLOP: (COMSAT) Why do you say that? Pre-charge?

9 HALPERT: Yes.

10 DUNLOP: Pre-charge will increase?

11 HALPERT: Yes, I said pre-charge.

12 DUNLOP: I don't think you mean that. I haven't
13 heard anything yet so far that indicated that the problem would
14 be solved by increasing the pre-charge.

15 HALPERT: I was referring to not only the loss of
16 capacity on either electrode, particularly the negative, but
17 also I didn't get a chance to continue saying that we had had
18 a fading of the negative also in which we would have to
19 increase our pre-charge.

20 DUNLOP: The only reason I jump on that is that
21 the comment "pre-charge" has been used a number of times
22 through this discussion and why do you pre-charge? It seems
23 to me that almost all the comments that have been made about
24 fading have dealt with some form of either large cadmium-
25 hydroxide crystals being formed which could not be charged or

1 some some problem with carbonate causing a loss of the use of
2 the material.

3 Our experience has been that if anything, we are
4 able to utilize more of the pre-charge with time. The part
5 that we are losing on our cells with time is not pre-charge.
6 We are actually able to discharge more of that pre-charge at
7 useful rate after one and a half or two years than we were
8 after the first 30 cycles, where we were not able to utilize
9 the material is in the discharge state; we are not able to
10 charge it.

11 I think this is a rather interesting point, although
12 I haven't really said very much about it, and I think I am a
13 little bit confused here as to why. My only understanding now
14 as to why we use a large amount of pre-charge is either to
15 reduce the pressure of the gas we build up or else to allow us
16 to discharge at high rate or at low temperature but it doesn't
17 seem to help our cells very much in terms of either carbonate
18 buildup or in terms of the fading effect.

19 GASTON: (Grumman) I agree with Jim Dunlop, it is
20 our feeling too that the pre-charge should be kept low rather
21 than high.

22 HALPERT: I guess I should not have brought the
23 pre-charge in at this particular time. I was really trying to
24 get back to the negative fading, and what I really wanted to
25 determine at this particular point was what we can do about the

1 negative fading.

2 We have heard some talk about expanders. Have
3 expanders been used on the type of cells that are used in the
4 semi-dry or semi-wet type of cells; and has it helped?

5 Secondly, we know that continuous cycling has
6 caused us to see a loss of capacity on the negative, it seems
7 to me, only when we are continuously cycling.

8 What happens if we do rest? Is there a loss of this
9 or is there a fading of the negative when we do have rest
10 between cycles? Is it something we are always going to be
11 stuck with or can we do something about it?

12 May I have some comments with regard to that?

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2 MAURER: (Bell Labs) I have several comments, that
3 have been piling up here.

4 One, I agree with Reed that the resistance to the
5 electrolyte will not account for all of the voltage increase
6 on charge but the voltage increase in charge consists of
7 several parts, one of which is resistance to the electrolyte,
8 one of which is an increase in voltage of the positive electrode
9 itself. Another part is the simple effect of the lower pH
10 of the electrolyte caused by the carbonation. These three go
11 together to give you this peculiar effect.

12 On Dunlop's comment, what I tried to show yesterday
13 was that the process of overcharging tends to oxidize any
14 cadmium metals present, whether it be the inactive, electro-
15 chemically inactive material or the pre-charge, or, of course,
16 the working cadmium and produce cadmium-hydroxide part of
17 which may be active and part of which may be inactive for
18 various reasons that we have discussed here.

19 Fritz tends to favor large crystals. I agree that
20 that is one process. The other process is simple isolation
21 of the material from any conductor. that is effectively close
22 enough. If you charged at perhaps extremely low rates for
23 extremely long times, you may be able to reach some of this
24 material.

25 So I think that pre-charge is still necessary in

1 electrodes of this design to keep the balance of the working
2 electrode in the useful range and that it need be present for
3 that reason only.

4 Oxygen recombination is improved with pre-charge
5 but you can improve it by other techniques as well which we
6 hope to have the paper from the labs describing in the not too
7 distant future.

8 The carbonate effect itself comes in in a number of
9 ways. One are these voltage effects we have been talking
10 about in the plateau. I don't think the carbonate per se is
11 responsible for the fading. It is the catalyst that increases
12 the rate of fading; it provides a mechanism for dissolution and
13 reprecipitation of the active material, so that with carbonate
14 the cadmium-hydroxide is more soluble than let's say the
15 cadmium specie is more soluble and hence can move around faster.

16 It itself is not responsble for the fading.

17 CARR: (Eagle Picher). I would like to ask a
18 question again. That is, in the discussions regarding long-
19 term like six months trickle charging even at low rates we have
20 heard that this permanently reduces capacity. Has this been
21 attributed to positive or negative?

22 HALPERT: Does anybody want to answer that?

23

24

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25

DUNLOP: (COMSAT) I might make one comment. Our

1 results show that you can recover, if you are trickle charging
2 for long periods of time, if you go through complete discharge
3 at a high rate, fairly rate, on the following cycles you
4 will have recovered most of -- you don't lose ampere-hours,
5 you seem to lose voltage. This is what is indicative of our
6 test results and this is recoverable by reconditioning.

7 CARR: (Eagle Picher) If Don Mains is here, he
8 reported also that they showed loss. I was wondering if he
9 had more data?

10 FORD: NASA-Goddard) I agree with Jim that it is
11 not a capacity -- ampere-hour capacity loss, but you are
12 dealing with a watt loss per unit time or watt-hour loss and
13 this is because you observe a lower voltage characteristic
14 initially on discharge and you also get a second plateau about
15 105 to 108 volts and we have seen as much as 60 percent of the
16 actual capacity on a Gulton 12 ampere-hour cell.

17 We actually obtained 15 ampere-hours of capacity
18 out of this cell after over 18 months of trickle charge; but
19 over 60 percent of that capacity was obtained below 1.1 volt.

20 One other comment: Steve Gaston yesterday showed
21 some trend in overcharge voltage characteristics. We are
22 looking at this in a little more detail and as most of you
23 are familiar, when you overcharge a cell at low temperature
24 at low rates you get at normal charge voltage a peak voltage
25 and you get a plateau voltage. One of the things we are

1 observing now is the first obvious change in the overcharge
2 characteristics is the peak. You will, typically, on a new
3 cell, referring to a 20 ampere-hour type cell, see a peak
4 early in life of about 150 to 151 with a plateau voltage
5 after four or five hours of overcharge of about 149 to 148.5.

6 But you see, and we have seen this within six
7 months, that the peak voltage will to about 154 or 155
8 indicating the peak voltage has changed as much as 60 to 70
9 millivolts; whereas, the plateau voltage which, again, out in
10 the overcharge region has only changed about 10 millivolts.

11 When you observe this over a period of time, if you
12 continue to look for this through periodic overcharges of 4
13 to 6 hours, what we normally run, you see that the plateau
14 voltage then starts rising and eventually you get to a point
15 where you peak the voltage and you don't see a plateau. And
16 at this point is when we have observed that you begin to get
17 some hydrogen generation.

18 I have seen the contrary to this on one test where
19 we had cell voltages as high as 162 with a C over 40 overcharge
20 at zero and we stayed there for 8 hours and never got any
21 hydrogen.

22 HALPERT: Ed, do you want to answer that?

23 GASTON: (Grumman) I just want to extend my
24 yesterday's paper on the effect of aging. The only change in
25 the whole 750 days which we have seen in characteristics are

1 the overcharge characteristics. The charge and discharge
2 profiles are the same. I certainly don't see the double
3 plateau effect which shows the presence of carbonate.

4 I just wanted to mention that.

5 HALPERT: On the same subject? Gross?

6 GROSS: (Boeing) Earl Carr asked a question on the
7 effects of trickle charging on the positive. There is a well-
8 documented test information in the literature showing that you
9 can get definite positive electrode degradation with trickle
10 charge.

11 It is also well known that trickle charge,
12 especially if the rates are high, can contribute to flaking
13 off and blistering of those positive electrodes. In addition
14 there is a mechanism of a higher valence which can be obtained
15 which is available as a capacity but only at very low discharge
16 rates.

17 CARR: Eagle Picher) Again, going into this
18 situation where, -- I am concerned about this irreversible
19 or not irreversible --

20 HALPERT: Temporary reversible --

21 CARR: Maybe. I am serious. This is interesting
22 because based on what we have discussed here, it seems to me
23 that we can get the capacity back; for example, if we are
24 concerned with large crystals of inactive cadmium-hydroxide,
25 we go to a long-term, low-rate trickle charge. Now if we have

1 capacity loss due to long-term trickle charge, we go to a
2 conditioning procedure of low discharge rate and high charge
3 rates.

4 I cannot remember reading where anybody has done
5 this. Maybe truly we can recondition these batteries.

6 DUNLAP: Just one quick comment. There is this
7 carbonage buildup probably enhanced by trickle charge. This
8 is all I want to say.

9 (Laughter.)

10 HALPERT: Okay. I have got to give Ed his chance.

11 MC HENRY: (Bell Labs) On the subject of the
12 capacity fading and the material that you cannot charge back
13 up or can discharge, I found that if you make a powdered
14 cadmium electrode, it has not capacity at all. You have
15 finely divided cadmium powder but you cannot discharge it.

16 If you make cadmium-oxide electrodes, you can
17 charge it up with 100 percent efficiency, but when you try
18 to discharge it you only get about 80 percent back.

19 Now, it seems to me that you are stuck with some
20 cadmium you can't discharge. I also have taken these things
21 and dissolved them in dilute sulfuric acid which very rapidly
22 dissolves cadmium but it doesn't bother nickel, not particularly,
23 and besides I weight the plaque afterward to find out if I
24 lost any nickel.

25 I get a great deal of hydrogen. You put this in a

1 little gas buret and you catch all the hydrogen that comes
2 off and the amount of hydrogen that you get just about matches
3 the capacity you didn't get.

4 On top of that Dean has just told us how you can
5 cook the dying electrode in oxygen and then you can charge it
6 back up and you get all kinds of -- you know, it now charges
7 a great deal more to hydrogen evolution than it did before;
8 so apparently you have oxidized some of the cadmium. You
9 cannot oxidize cadmium-hydroxide.

10 If you have oxidized cadmium, it was because it was
11 cadmium and not cadmium-hydroxide. It must have been there as
12 metal. You heat it in oxygen, wet oxygen, and you now oxidize
13 it, and you can use it again. Of course, it fades very
14 quickly afterward but it seems to me that you can get cadmium
15 which cannot be oxidized. I think you can also get cadmium-
16 hydroxide that will not reduce, but I think the metallic
17 cadmium that apparently is isolated or something from the metal
18 structure is a problem.

19 It is not a case of only cadmium-hydroxide which is
20 inactive.

21 HALPERT: Does anybody else want to comment about
22 a particular subject.

23 I think at this particular point -- okay, Dean
24 Maurer.

25 MAURER: (Bell Labs) On the matter of long-term

1 trickle charge being detrimental, I think that this has gotten
2 to be taken slightly out of context.

3 What was said, as I remember it, was that two
4 groups of cells, one which was left on open circuit and one
5 which was trickle-charged for a year, when tested, acceptance
6 tested at the end of this time, the ones on long-term over-
7 charge showed lower capacity than those that were left on open
8 circuit.

9 Now part of this could be simply that the ones on
10 long-term overcharge had been working and so you are seeing a
11 wear-out; whereas, the ones on open circuit were simply
12 standing idle. So part of this can simply be attributed to
13 the working of the cell; that is useful performance of the cell
14 versus a real difference in characteristic, if you follow what
15 I mean.

16 At the end of this period of time one group of cells
17 is essentially unaged; they have been sitting on the shelf;
18 and the other group has seen a year's work.

19 CARR: (Eagle Picher) But they all have the same
20 amount of material in them that they had in the beginning.
21 What is the way out?

22 MAURER: (Bell) I agree the wear-out has taken
23 place.

24 CARR: Yes. What is it?
25

1 FLEISCHER: (Consultant) A long time ago I trickle
2 charged a 40 ampere-hours sintered plate battery which had
3 string separators so that it had no cellulose in it. It was
4 fully flooded. The trickle-charge voltage was 1.40 and it was
5 kept that way for a year.

6 The trickle-charge current was somewhere around 10
7 milliamperes. It actually generated gas which was equivalent
8 -- the gas was measured and the overall gas at the end of one
9 year was about 20 percent of the theoretically expected amount
10 of hydrogen and oxygen.

11 At the end of the year, the cell was discharged and
12 it gave a capacity of 44 ampere-hours instead of the 40
13 ampere-hours which it gave on numerous cycles prior to the time
14 it went on trickle charge.

15 It never went back to 44; after that it cycled again
16 at 40 ampere-hours. But I want to call your attention to the
17 fact that in the flooded state the trickle charge voltage is
18 1.40 and this is also a high value for the pocket-type electrode
19 which has electrolyte that has a density of 1.20 to 1.23; so
20 we have a very high trickle-charge voltage on these cells,
21 way above where they ought to be for sintered-plate batteries.

22 HALPERT: Can I ask for the record what it should
23 be for sintered-plate batteries?

24 FLEISCHER: With a flooded cell I said it was 1.40.

25 HALPERT: Okay.

1 LACKNER: (Canadian Defense Research Labs) (DRE
2 Canada). We have gone over the long-rate trickle charge and the
3 fading. We have had some experience with that and we have said
4 that it is not irreversible, that you can get back to capacity.

5 Dean Maurer said that the cells that have been on
6 trickle charge for a long period of time were working. These
7 cells were not working. You were overcharging them but if you
8 really want to exercise them, at periodic intervals you should
9 discharge the cells down to at least one volt or less and the
10 periodic interval should be about three months.

11 And then you will really be -- when you work a cell
12 you discharge it and charge it. The ni-cad system is noted
13 for being able to work many cycles of long life, so it should
14 not have a wear-out.

15 HALPERT: Dr. Will?

16 MAURER: Can I answer that?

17 HALPERT: All right.

18 MAURER: (Bell) A battery in a reserve mode, like
19 a night watchman, sits around and waits for something to happen;
20 and in that context the battery in reserve operation on trickle
21 charge can be working.

22 (Laughter.)

23 WILL: (G.E.) We seem to be agreeing more and more
24 that trickle charge may be detrimental to the nickel plate, to
25 the positive plate, and that it may not be detrimental at all;

1 it may be in fact beneficial to the negative plate.

2 I would like to amplify on that latter point once
3 more in saying that what one is doing with trickle charging
4 the negative plate is to cathodically protect the negative
5 plate and thereby not allow dissolution and the dissolution is
6 obviously the major mechanism causing the fading of the negative
7 plate.

8 I would, therefore, like then to pose the question
9 to the experts on the positive plate, and would challenge them
10 in coming up with some possible mechanisms of failure modes of
11 positive due to the trickle charge.

12 HALPERT: Dr. Himy down here has a comment. I hope
13 you are going to answer it.

14 HIMY: (McDonnell) I want to go back to the problem
15 of carbonate built up in the cell. If part of the problem
16 in fading or otherwise in nickel-cadmium cells is due to con-
17 centration of carbonate build-up, due probably to the decay of
18 organic membrane, whether they are cellulose-zinc or nylon,
19 it just seems natural to go back to inorganic membranes.

20 It is not the cell's fault here, I tested some
21 cells of silver-cadmium with inorganic materials and I cannot
22 say I noticed any fading because the cell was designed with
23 excess negative ratio, negative to positive ratio, as usual.

24 The cells have so far reached 6,000 cycles at 40
25 percent depth of discharge and are still going strong, so

I couldn't say, really, if there is any fading; that means it it probably still above the level of the 1 to 1 ratio.

STEINHAURER: (Hughes) I would like to comment in reinforcement of some of Jim Dunlop's statements.

We have been running parallel testing on the IntelSat-4 program and one of my colleagues, Al Heller, is on that program. In synchronous earth orbit we have 135 days' storage period between eclipse seasons and we have been through one eclipse season and one storage mode into the second eclipse season and we may be a little farther along than that, I am not sure.

The point is that that satellite has several -- three modes of charge where we could trickle charge if we wanted. The results on trickle charge indicate some of the things that Floyd has pointed out and that Jim has pointed out, namely, that you get a voltage drop in the voltage curve versus run time or ampere-hours.

We haven't seen it plateau out yet; just a soft knee, but this is recoverable by a big discharge down to about somewhere in the range of 120, 115 volts per cell, and we have seen this on other programs, so it is apparently recoverable.

HALPERT: Is anyone going to comment about the positive electrode, Dr. Will's question? It would be kind of interesting here.

BEAUCHAMP: (BTL) I presented just a little data

1 yesterday on trickle charge of six months at 50 degrees F. and
2 there was no second plateau. I got full capacity out of the
3 cells. At higher temperatures we started to see an initial
4 plateau.

5 I don't know the answer to Earl's question, whether
6 it is the negative or the positive, since we didn't have
7 reference electrodes in the cells. It was my thought though
8 that it was probably due to the negative plate on this long
9 trickle charge, possible growing larger cadmium crystals.

10 The positive plate, I think, if you do X-ray
11 diffraction work, is very amorphous, very small crystals; so I
12 have no direct measurement but I just think it negative.

13 DUNLOP: (COMSAT) Whose cells were they?

14 BEAUCHAMP: The data was marked on those graphs
15 yesterday; I forget exactly whose were different temperatures.
16 I think I had three manufacturers and I would have to go back
17 and really go through the data to say whose cells did what.

18 We have tested Eagle Picher, Gulton and G.E. cells.

19 HALPERT: Okay, any other comments? Dean?

20 MAURER: (Bell) I would like to comment on the
21 peak you see in the charging curve.

22 This peak is a function of the cell design; cells
23 can be designed and, in fact, some commercial manufacturers
24 produce cells that have no peak on the charge curve, the
25 transition from charge to overcharge shows no peak. This, in

1 fact, was part of the controversy over the various rapid
2 charging systems that were ballyhooed six months or a year
3 ago that depended on increase in voltage to turn the rapid
4 charge off.

5 Some manufacturers' cells do not have this peak.
6 The peak results from the effect of oxygen being generated
7 at the positive electrode near the end of charge. The first
8 thing this oxygen does is increase pressure in the cell.
9 It comes out through the separator, fills the void spaces,
10 and increases in pressure.

11 Finally it gets to the negative electrode where it
12 depolarizes it. The voltage -- the topple voltage of the
13 cadmium electrode is a function of the oxygen pressure and as
14 the oxygen pressure goes up the cadmium voltage goes down so
15 that the first thing you see as you reach near the end of
16 charge is the voltage in the cell goes up because both
17 electrodes are reaching higher states of charge. And then as
18 the pressure increases in the void spaces of the cell, the
19 voltage starts to drop back down again and eventually reaches
20 an equilibrium condition where the recombination rate on the
21 negative electrode equals the charging rate. And at that
22 point pressure rise stops and the voltage stabilizes.

23 Just as an example, a cell with a larger void
24 volume would probably have a bigger peak than a cell with a
25 smaller void volume. Also, a cell that has a negative that is

1 inherently faster at recombination, will have a lower charging
2 peak or maybe no peak at all, than an electrode which is less
3 efficient at recombination.

4 I want to emphasize that the recombination rate is
5 always the same because we are in an equilibrium condition,
6 a closed system. The recombination rate always equals the
7 charge rate after you have once gotten into the overcharge
8 region.

9 Your comment was that a cell which initially had
10 one type of voltage peak after aging, now had a new type
11 could be explained by some of these cadmium specie migrations
12 that we have been discussing here. If, for example, the pores
13 of the negative electrode became clogged at the surface because
14 of cadmium, cadmium-hydroxide, or cadmium-carbonate
15 accumulation there -- and many of us have seen that in cells
16 that have been dismantled -- there is a lot of material on the
17 surface of these plates -- then the recombination rate on those
18 electrodes is very likely -- sorry, the recombination efficiency
19 is likely to be poorer because the pores are now blocked.

20 Then you would expect that you would see a higher
21 peak in a cell of that sort than you would without the pores
22 being clogged.

23 FORD: It might make you feel better, one of the
24 characteristics that has been observed in the cell under the
25 same overcharge condition is that comparing the early life with

1 the later life, and we are talking about 3,000 cycles now, at
2 a temperature of about 55 degrees F. The steady state over-
3 charge pressure is built up about 20 to 30 percent. But one
4 thing that puzzles me about this, and statistically we don't
5 have that many numbers, but the numbers we do have where we have
6 gotten into a very unusual high voltage characteristic, and run
7 the wet plate test on the cells, we have always found or
8 found a correlation with the fact -- well, two things -- one
9 is that the positive plate capacity has increased and it is
10 increased because it is above what we know the positive plate
11 capacity of this plate lot was early in life; two, the negative
12 plate capacity is always very close to the positive plate
13 capacity.

14 In some cases, and I think Gerry completed some
15 work on the plates from these cells, we find ratios of about
16 1.1 to 1; and we find ratios of 1.0 to 1, and we have even had
17 ratios -- negative ratios if you want to call it that -- but
18 I realize there are probably other factors like carbonate and
19 so forth that are giving us this problem.

20 On the other hand, it always show up in tests that
21 we know how to run, at least, the wet electrode capacity test,
22 as low, negative capacity; and I am talking about a loss of
23 cells that start off with a ratio of 1.40, 1.5 to 1, which means
24 you have roughly about 40 ampere-hours of capacity in these
25 cells after 3500 cycles now have 31-32 ampere-hours capacity.

1 And I am not saying it cannot be recovered; I think
2 maybe Gerry might comment on that because he has been running
3 some individual plate tests on these type cells.

4 HALPERT: On those particular plates from those
5 cells, we took two cells from the group that have been cycled
6 for six months, as Floyd said, and two that have not been, and
7 took representative plates from both groups.

8 Just as he said, the electrochemical capacity of the
9 positives was slightly higher and the electrochemical of
10 the negatives was low by approximately 0.6 ampere hours out of
11 3.5 ampere hours per plate. And even though we gave them 75
12 percent overcharge in flooded condition, we could not get the
13 capacity back out again. So it was not recoverable.

14 Maybe if we had done it at 5 C rate or something and
15 discharged it, it might have happened differently; but it was
16 obvious that the capacity was gone.

17 Now, whether that means that the chemical structure
18 of the plate is different, has more cadmium than cadmium-
19 hydroxide, or some other compound in which we have lost the
20 weight, or whether it is actually material lost by going into
21 the separator, I cannot determine at this point.

22 GROSS: (Boeing) Overcharging would take inactive
23 cadmium and convert it into active cadmium; however, the cells
24 are not made with great uniformity and are not made in a way

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1 that we can allow easy access of oxygen to the interior of the
2 plate during overcharge; consequently, the overcharge reaction
3 occurs preferentially on the outside exposed edges of the
4 plates.

5 I would speculate that this would allow the inactive
6 cadmium species in the interior of the plate to not get
7 regenerated but I have no facts to go on. I wonder if anybody
8 knows whether this is the case.

9 HALPERT: The plates that we looked at in that
10 particular group were almost a clay-like structure covering the
11 surface. We didn't go to very, very high magnification, but
12 in the scanning electron microscope we couldn't see below the
13 surface.

14 The covering was like a clay. Plates of the same
15 type from the same batch that were put into the like cells and
16 allowed to stand for the six months' period did have pretty
17 open structure that we could see into. They had been given
18 one or two cycles, the plates that had been standing and had
19 gone through a manufacturer's testing program.

20 They were just set aside at that particular point
21 and left. So, the fact that there was a covering indicates
22 that it may have been a problem of oxygen getting into the
23 inner area, if that is what you are saying.

24 GROSS: Well, I am commenting on the general question
25

1 of what is the effect of trickle charge.

2 HALPERT: This didn't have anything to do with
3 trickle charge, on the plates that Floyd was talking about;
4 these were on continuous cycle for six months at Crane in a
5 simulated 25 percent depth orbit.

6 GROSS: My speculation is that trickle charge would
7 not be fully effective in recovering the lost capacity on the
8 passivated cadmium. I am questioning whether anybody knows
9 whether this is the case or not.

10 HALPERT: Dunlop?

11 DUNLOP: I don't want to answer that question so I
12 will let somebody else have the floor.

13 HALPERT: Does anybody want to answer it? Dr. Will?

14 WILL: G.E.) It is true that the dissolution of the
15 cadmium-hydroxide crystals start at the pore mouth. It is
16 also true that these big cadmium hydroxide crystals did
17 originally block the pores. As soon as these crystals are
18 dissolved the blockage stops and the field can penetrate
19 farther into the pore and consequently the cadmium-hydroxide
20 crystals further inside the pore finally also dissolve.

21 However, this is a slow process.

22 May I make one point on the gas evolution and the
23 oxygen evolution in the overcharge mode?

24 This process is a diffusion limited process and the
25 oxygen will not cause the potential of the cadmium electrode to

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1 drop. If anything, as the pressure rises of the oxygen in the
2 sealed cell, the potential of the cadmium electrode is going to
3 become more positive. It is bound to happen; there is no
4 other possibility.

5 MAURER: We don't see that in practice.

6 WILL: Then there must be a different reason for it.

7 (Laughter)

8 HALPERT: We have a small disagreement over here.

9 DUNLOP: (COMSAT) I just want to go back and ask a
10 question about your work there, Gerry.

11 When you observed the loss in capacity, did you go
12 through a chemical analysis on the plates?

13 HALPERT: Yes, we did go through extraction, samples
14 taken from the same lot before they were cycled. After we
15 removed them and cycled them, we took sample plates, then we
16 did a chemical extraction and electrochemical testing.

17 DUNLOP: Were you able to determine whether your
18 problem was charging the cadmium or discharging the cadmium?
19 If you did both electrochemical and chemical analyses, you
20 should have been able to determine if it was one or both.

21 HALPERT: No, the capacity was significantly
22 reduced about 0.6 ampere hours out of 3.5 ampere hours.

23 DUNLOP: I understand that, but was it the fact
24 that you couldn't discharge it, with the metallic cadmium there
25 you could not discharge at a useful rate or you couldn't

1 discharge or you could not charge the cadmium hydroxide?

2 HALPERT: We charged at 75 percent overcharge and
3 we could not get the capacity out of plates that were in the
4 same line, operated at the same time, from the new cell.

5 DUNLAP: I understand you did not get the capacity
6 out.

7 HALPERT: Yes.

8 DUNLAP: Now, I am asking you the question, was it
9 the fact that you could not charge it or the fact that you could
10 not discharge it? Do you know?

11 HALPERT: I really don't remember. It was done
12 elsewhere. I don't remember the numbers. Don, would you
13 happen to remember the numbers offhand?

14 VOICE: I cannot remember them.

15 HALPERT: Okay, I don't have the numbers with me.
16 I cannot remember that.

17 DUNLAP: This really is a rather important point
18 because there is a lot to do with this whole business of
19 pre-charging and everything else. You really ought to find
20 out whether it is a problem of being able to charge the
21 cadmium or whether it is a problem of being able to discharge
22 the cadmium. And if you do a complete analysis, you know, this
23 is the point that we were making yesterday in the paper: If
24 you do go to an analysis where you do both an electrochemical
25 and a chemical analysis of your plate, then you can, indeed,

1 determine which problem you are having, if you are losing
2 utilization of the plate, whether it is a problem of charging
3 the plates or a problem of discharging the plates.

4 HALPERT: These data are available.

5 CARR: (Eagle Picher) There is a third possibility.
6 That is whether it is there or not.

7 DUNLAP: He mentioned a loss of weight. I agree,
8 but he mentioned a loss of weight of about 25 percent. He
9 mentioned a loss of capacity of about 50 percent, so there was
10 a loss of capacity which exceeded the loss in weight that he
11 mentioned. As I understood it, I may be wrong there.

12 STEINHAUER: (Hughes) Maybe we shouldn't get into
13 this question, but --

14 (Laughter.)

15 STEINHAUER: -- there has been the point made of
16 surface charge versus diffusing the charge into the plate.
17 There are several people in the room, I think, that have done
18 pulse charging but more particularly I would like to direct
19 my questioq toward pulse trickle charging. I believe the
20 Canadians', Army Electronics and perhaps Utah Research have
21 some work on this.

22 Can we live with the cells as they stand with the
23 carbonate? Does the capacity and voltage hold up under pulse
24 trickle charging over a long time?

25 HALPERT: Lackner?

1 LACKNER: (Canadian Defense Research Labs) I
2 imagine that question was directed to me, wasn't it?

3 Are there any other Canadians here?

4 (Laughter.)

5 LACKNER: We have done tests on pulse trickle
6 charging and pulse high-rate charging; and we have found that
7 if you charge at a high rate you get better charge efficiency.
8 I believe this was already known.

9 If you pulse charge at a high rate, and then when
10 you get into the overcharge period, which would normally be
11 your trickle charge, if you then still pulsed at a high rate
12 but a low average charge rate -- in other words you spread out
13 your pulses -- you could maintain the capacity for a long
14 period of time on the order of a year.

15 We have done this on standby emergency lighting
16 units. We still feel that you have to exercise the battery
17 because if you continue it in one mode, it develops a certain
18 condition and I hate to mention the word memory --

19 (Laughter.)

20 LACKNER: -- How it develops this condition I won't
21 enter into it. I believe Dr. Will has exhausted that topic.
22 But you have to prevent it from getting into a certain mode,
23 so you do have to exercise it.

24 What the pulse does, it exercises it to a certain
25 extent.

1 HALPERT: Let me make a point here.

2 We ought to be finishing up in the next five or
3 ten minutes. I know some of you still have to travel this
4 evening so --

5 BOYD: (Utah Research) We have been pulse charging
6 about five or six years now, approximately. We have been
7 noticing something occurring. We have not done a lot of
8 trickle charging, so I cannot answer all of your questions, but
tape 5 9 we have noted if a battery cell is faded, caused by a short
6 LRW 10 -- cycle, the pulse charge does remarkably well in restoring
11 capacity.

12 But if, on the other hand, it is caused by a
13 deep cycle or a heavy cycle, then we don't do as well. We have
14 to have this periodic recycling down to zero or 1 volt per cell.

15 Most of our work has been on the vented ? cells so
16 we haven't got a lot of history on the sealed type cell.

17 By the way, we also should make a comment that the
18 type of pulse is very critical. If you have a high peak of
19 average ratio, then you do have some degradation caused by
20 heating the cell; but if you maintain say a 2 or 3 times the
21 average peak ratio, then you do very well. So all of these
22 things must be considered.

23 We have about five different types of types of
24 pulse charges we built currently, one of which has a burst
25 effect wherein we have, I believe it is a six peaks per burst

1 at the actual frequency of input voltage, and this does very
2 well. But as we go to a single pulse and have a very high
3 ratio we only have degradation occurring, so some caution must
4 be used in pulse charging. But it is also very beneficial.

5 MAURER: (Bell) I would like to make a few comments
6 about this and the negative electrode.

7 First of all, the negative electrode potential is
8 a mixed potential. It consists of the hydrogen potential,
9 the cadmium potential and the oxygen potential. Relative
10 to a mercury reference, the oxygen potential is positive; the
11 cadmium potential is negative by about .9 volts or something
12 of that sort; and hydrogen potential is negative by about
13 1.1 volts.

14 This potential is mixed which means that in any
15 given situation all three reactions can occur. So the presence
16 of oxygen will tend to make the potential go more positive
17 than it would if it were not in the presence of hydrogen
18 the other way. So in an overcharging electrode one would
19 expect tht the oxygen would depress the negative potential,
20 that is, make it more positive than it was in the first place,
21 which tends to decrease the voltage.

22 The other point I wanted to make was that pulse
23 trickle charging -- I have no experience with this per se, but
24 I do have some experience with what we call interrupted
25 overcharge, and this is definitely detrimental to the cell when

1 the interruption is of an order of time comparable to the
2 time it takes the oxygen pressure -- that is, the equilibrium
3 oxygen pressure on overcharge -- to decay to appreciably lower
4 values. When charge is returned and after this period of time
5 oxygen is not present so the inherent potential of the negative
6 electrode is higher and you tend to generate hydrogen, so that
7 if you interrupt an overcharge, specially at low temperatures,
8 for periods of time let's say on the order of 15 minutes to an
9 hour, you will get appreciatble quantities of hydrogen when
10 the charge is started again.

11 If the interruption is of short duration, in
12 seconds or minutes, there is no appreciable effect,

13 CARR: What rate?

14 MAURER: C over 20.

15 DUNLOP: I just have one comment. About 1968,
16 at the IEEE, I published a paper there on the pulse-charging
17 work that we did for about a year and a half or so in the labs.
18 What we did, we took a group of third~~?~~electrode cells, either
19 third electrode for charge control, and we took two packs and
20 we pulse-charged one pack and we constant-current charged
21 another pack at the same average rate. And we tried different
22 duty cycles on the pulse rate -- 10 percent, 15 percent, 20
23 percent and so forth. We tried different rates, C over 5
24 average, C over 10, C over 20.

In all that work, and you can find that reference,

1 it took the same amount of time, using the same average current,
2 to charge a cell up whether you do it with pulse charging or
3 whether you do it with constant-current charging at the same
4 average rate.

5 This is an ampere-hour charge efficiency that I am
6 talking about. You don't improve the ampere-hour charge
7 efficiency.

8 For the 900 cycles that we ran, wherein we were
9 using, I believe it was, a C over 25 percent duty cycle and
10 an average C over 10 charge rate, we used an 80 percent depth
11 of discharge, we had the same basically at the end of the 700
12 or 800 cycles, whatever it was, the discharge characteristics
13 of both packs looked almost identical. We reconditioned both
14 packs and they still looked almost identical.

15 So, for that period of time, we were not able to
16 determine that there was either an advantage or a disadvantage
17 to the pulse charge.

18 HALPERT: Boyd, Utah?

19 BOYD: (Utah Research) We have seen much the same
20 thing, except in some cases. We have noticed, by taking some
21 cells a degrading of perhaps 30 to 40 percent. In some cases
22 the first charge cycle with pulsation they recover completely.
23 With constant current that isn't true; however, there are some
24 cases where neither recover, either pulse or constant current.
25 And, again, we find a correlation, basically first with the pulse

1 wave itself.

2 If we hold the pulse peak constant, at the duty
3 cycle, then we don't have any improvement. But if we vary
4 the peak and the duty cycle both, we do find improvement
5 occurring.

6 And then, secondly, as I mentioned before, if the
7 fading is caused by shallow cycling, then we have good results.
8 But if it is caused by deep cycling or heated cells, there is
9 no recovery.

10 HALPERT: At this point I might say that we have had
11 a very productive session. I think we have covered some of the
12 areas that Chuck McKenzie suggested we cover back in his
13 beginning keynote address, and I hope that all of you have
14 enjoyed it and gotten something out of it.

15 We hope to have the proceedings back to you in as
16 short a time as possible, on the order of three weeks to a
17 month. And I hope that all the slides will be in so that
18 we will have them to accompany it.

19 I do want to make mention of the fact that we have
20 had some foreign visitors with us here today and yesterday --
21 Drs. Font and Perrachon from SAFT sitting right over here; and
22 in the back row we have Ferguson from Canadian Arsenals and
23 Stott from Telesat, Canada; and you have met Joe Lackner of
24 Canadian Defense Research Labs. We are very happy to have had
25 them come down and visit with us.